CHEMICAL ENGINEERING TRANSACTIONS
VOL. 45, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216
DOI: 10.3303/CET1545198

Optimal Processing of Carbon Nanotubes

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This paper presents an optimisation approach for determining the best synthesis method and their corresponding operating conditions for synthesising carbon nanotubes for a desired application accounting for technical and economic issues as objective functions. Proper correlations for the interaction between the considered variables are proposed, and these correlations are based on experimental data obtained in the lab. The optimisation formulation is a mixed-integer nonlinear programming problem. A case study considering three synthesis methods of carbon nanotubes (arc discharge, laser ablation and chemical vapour deposition) is presented. High-temperature techniques such as electrical arc-discharge and laser ablation produce CNTs with the highest quality in terms of the graphitic structure; however these techniques are slow and expensive, while the CVD technique is able to produce extremely dense and pure materials, and properties such as crystal structure, surface morphology and orientation of the products can be manipulated and customised via the CVD's process parameters. The results show that the proposed model can be useful to determine the best method and operating conditions with the maximum efficiency, quality and safety at the minimum cost.

1. Introduction

Carbon nanotubes (CNTs) are one of the most exciting discoveries in nanoscale sciences because they have superior properties with respect to other materials in several applications (Ng et al., 2013). Since the discovery of CNTs, a variety of techniques for their production have been developed, where numerous key parameters and operating conditions have to be manipulated to yield CNTs with the desired final properties (Mubarak et al., 2014). Among these techniques are the electric-arc discharge, laser ablation and chemical vapour decomposition (CVD), where different structures of CNTs can be produced in the form of vapour grown, carbon fibre and different types of carbon nanostructured materials (Liu et al., 2014).

Mubarak et al. (2014) carried out different experimental researches, where the simultaneous interactions between the manipulated variables have not been optimised to yield the desired properties, and specific targets such as the production of CNTs with the minimum cost, minimum environmental impact and minimum risk have not been considered. In this context, Hernández-Vargas et al. (2013) recently reported an optimisation formulation for the synthesis of nanofibers at the minimum cost, where the importance of taking into account these types of objective functions is highlighted. On the other hand, safety in chemical processes is another very important factor that is rarely taken into account as a key parameter to propose new strategies to obtain new materials (Schmidt, 2013). Therefore, in order to account for a proper methodology for identifying the optimal synthesis and operating conditions for yielding CNTs with desired properties, this paper proposes an optimisation formulation based on experimental correlations to determine the optimal synthesis method and operating conditions for producing CNTs accounting for technical, economic and safety issues. The optimisation formulation is based on a mathematical programming formulation that considers several variables and objectives as shown in Figure 1.

Please cite this article as: Hernández-Vargas J., Martinez-Gomez J. , González-Campos J.B., Lara-Romero J., Ponce-Ortega J.M., 2015, Optimal processing of carbon nanotubes, Chemical Engineering Transactions, 45, 1183-1188 DOI:10.3303/CET1545198

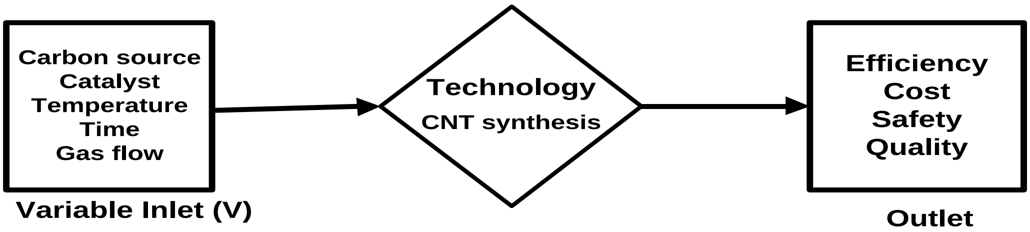

Figure 1: Interrelations for yielding CNTs with desired properties for specific applications

1.1 Proposed optimisation formulation

This paper proposes a disjunctive programming formulation to select the type of technology used *(t)* as well as the operating parameters *(V)* including the weight of carbon source, weight of catalyst, temperature, time and flow rate of the carrier gas for synthesizing carbon nanotubes determining the efficiency *(Eff),* cost of production *(Cost)*, safety of the process *(Saf)* and quality of the obtained products *(Qualy)*. The proposed disjunctive formulation is stated as follows:

$$\bigvee_t \left[\begin{array}{c} Y_t \\ Eff = f_t^{Eff}(V_U) \\ Cost = f_p^{cost}(V_U) \\ Saf = f_t^{Saf}(V_U) \\ Qual = f_t^{Qual}(V_U) \\ V_{U,t}^{\min} \le V_U \le V_{U,t}^{\max} \quad \forall_U \in U \\ \end{array}\right]$$

In previous formulation, Y_t is a Boolean variable that is true when the technology t is selected as the optimum one, and for this case the corresponding relationships for the efficiency, cost, safety and quality are applied. In the case when the Boolean variable Y_t is false, the relationships are not considered. It should be noted that for each technology there are specific relationships for the diameter and cost as well as limits for the involved variables. In addition, only one technology must be selected as the optimal one. Then, previous disjunctive formulation must be reformulated as a set of algebraic relationships to be implemented as a formal mathematical programming formulation (Gutiérrez-Arriaga et al., 2013). This way, to state that only one technology can be selected (i.e. only one binary variable y_t must be one) the following Eq(1) is used:

$$\sum_T y_t = 1 \tag{1}$$

Then, the relationships to determine the efficiency (*Eff*) for the process must be stated only for the selected technology t as follows:

$$f_t^{Eff}(V_U) - M^{Eff}(1-y_t) \le Eff \le f_t^{Eff}(V_U) + M^{Eff}(1-y_t), \qquad \forall_T \in t \tag{2}$$

where M^{Cost} is a big-M parameter used to activate the corresponding efficiency. When the technology t is selected, then the binary variable y_t is one and the last terms of Eq(2) are zero. This means that the associated cost has to be calculated according to the relationship for the technology t ($f_t^{Eff}(V_U)$). On the other hand, when the technology is not selected, the binary variable y_t is zero and the last terms of Eq(2) are M^{Eff} and $-M^{Eff}$. Notice that for this case these terms M^{Eff} and $-M^{Eff}$ relax Eq(2); this means that the cost is not calculated using the corresponding function for this technology.

Then, the relationships to determine the cost (*Cost*) for producing carbon nanotubes must be stated only for the technology t selected to be the optimum one as follows:

$$f_t^{Cost}(V_U) - M^{Cost}(1-y_t) \le Cost \le f_t^{Cost}(V_U) + M^{Cost}(1-y_t), \qquad \forall_T \in t \tag{3}$$

The relationships to determine the safety of the process are stated as follows:

$$f_t^{Saff}(V_U) - M^{Saff}(1-y_t) \le Saff \le f_t^{Saff}(V_U) + M^{Saff}(1-y_t), \qquad \forall_T \in t \tag{4}$$

The quality of the obtained product is given by Eq(5):

$$f_t^{Qual}\left(V_U\right)\text{-}M^{Qual}\left(1-y_t\right) \le Qual \le f_t^{Qual}\left(V_U\right)+M^{Qual}\left(1-y_t\right), \qquad \forall_T \in t \tag{5}$$

Notice that the limits for the variables involved depend on the type of selected technology, and because the type of technology is an optimisation variable, then this is modelled as follows: first there are upper (V_U^{up}) and lower (V_U^{lo}) limits for the involved variables *U*; however, these limits are optimisation variables that are determined depending on whether the technology is selected or not. This is stated as follows:

$$V_U^{lo} \le V_U \le V_U^{up}, \qquad \forall_U \in U \tag{6}$$

where these lower and upper bounds are determined as stated in Eq(7) and Eq(8):

$$V_U^{lo} = \sum_t V_{t,U}^{\min} y_t, \qquad \forall_U \in U \tag{7}$$

$$V_U^{up} = \sum_t V_{t,U}^{\max} y_t, \qquad \forall_U \in U \tag{8}$$

In previous relationships, V_U^{up} and V_U^{lo} are lower and upper limits for the variable *U* associated to the technology *t*. Notice that the variables V_U^{up} and V_U^{lo} are equal to the one of the selected technology because for this case the binary variable is activated. Table 1 shows the considered variables of the process. A set of correlations, based on experimental data (Liu et al., 2014) were obtained using the Statgraphics software. By a multiple regression analysis, a polynomial equation was found; it shows a relationship between the dependent variable (efficiency, cost and safety) and independent variables [initial weight of carbon source (g), weight catalyst (g), temperature (°C), gas flow rate (mL/min) and time (min)].

1.2 Case study

High-temperature techniques such as electrical arc-discharge and laser ablation produce CNTs with the highest quality in terms of the graphitic structure; however these techniques are slow and expensive (Prasek et al., 2011), while the CVD technique is able to produce extremely dense and pure materials, and properties such as crystal structure, surface morphology and orientation of the products can be manipulated and customised via the CVD’s process parameters, however, this process includes inherent chemical and safety hazards caused by the use of toxic, corrosive, flammable, and/or explosive precursor gases. Prasek et al. (2011) analysed the parameters that influence the growth mechanism of CNTs as the catalyst, carrier gas type and flow rate, substrate, synthesis temperature and reaction time. The authors determined that the most effective and widely used catalysts are the Fe/Co/Ni based because of the high solubility of carbon in these metals at high temperature and the high carbon diffusion rate in these metals. Glaser (2012) showed that typically nanometer-size metal particles are required to enable hydrocarbon decomposition and the growth rate of CNT depends on the catalyst particle size and the diffusion rate of carbon through the catalyst; the higher the catalyst particle size, the lower the growth rate, while the growth rate of CNTs is directly proportional to the diffusion rate of carbon through the catalyst. He demonstrated that the most used CNT precursors are methane, ethylene, acetylene, benzene, xylene, carbon monoxide and botanic source and the carrier gas also affects the growth of CNTs, and mainly H_2 and Ar are used. In this paper we studied three technologies for synthesising carbon nanotubes; these are arc discharge, laser ablation and chemical vapour deposition, where in the latter two carbon sources were analysed (camphor and turpentine). For each technology a correlation between cost and efficiency as function of initial weight of carbon source (g), weight catalyst (g), temperature (°C), gas flow rate (mL/min) and time (min) was obtained and it is shown in Table 1. Table 2 shows the carbon source, catalyst and flow gas for each technology analysed, and in the Table 3 the correlations of each technology studied in this paper are shown.

Table 1: Variables for carbon nanotubes synthesis for the presented case study

Independent variable	Process parameter
v_1	Weight of carbon source, g
v_2	Weight of catalyst, g
v_3	Temperature, °C
v_4	Gas flow rate, mL/min
v_5	Time, min

Table 2: Carbon source, catalyst and flow gas for each technology

Technology	Carbon source, g	Catalyst, g	Flow gas, mL/min
Arc discharge	3.75	2.755	200
Laser ablation	0.67	0.001	400
CVD camphor	0.10	0.035	40.0
CVD turpentine	4.00	0.107	10.0

Table 3: Correlations between cost and efficiency of each technology

Technology	Correlation for efficiency	Correlation for cost
Arc discharge	$Eff = -20.5048 + 45.3291 \bullet v_2 + 0.0258 \bullet v_3 + 0.0553 \bullet v_4 + 0.2602 \bullet v_5 - 0.8614 \bullet v_1 \bullet v_2 - 0.0154 \bullet v_2 \bullet v_4$	$TotCost = 0.0042 \bullet v_1 + 1.106 \bullet v_2 + 0.032 \bullet v_4 + 0.002 \bullet v_5$
Laser ablation	$Eff = 32.16 + 856.77 \bullet v_1 + 71369.4 \bullet v_2 - 216.889 \bullet v_2 \bullet v_4 - 40.2681 \bullet v_2 \bullet v_3 - 5.5714 \bullet v_1 \bullet v_5$	$TotCost = 0.0042 \bullet v_1 + 0.810 \bullet v_2 + 0.032 \bullet v_4 + 0.003 \bullet v_5$
CVD camphor	$Eff = -63.9175 - 3.03707 \bullet v_1 + 50439.6 \bullet v_2^3 + 23303.8 \bullet v_2^2 + 3056.96 \bullet v_2 + 0.0572793 \bullet v_3 + 0.513682 \bullet v_4 - 2.32872 \bullet v_5$	$TotCost = 0.023 \bullet v_1 + 0.273 \bullet v_2 + 0.032 \bullet v_4 + 0.0015 \bullet v_5$
CVD turpentine	$Eff = 116.273 - 61.6575 \bullet v_1 + 1665.57 \bullet v_2 + 0.053 \bullet v_3 - 1.102 \bullet v_4 + 4.66 \bullet v_5$	$TotCost = 0.003 \bullet v_1 + 0.273 \bullet v_2 + 0.032 \bullet v_4 + 0.0015 \bullet v_5$

The presented model also takes into account the analysis of the safety of different technologies for the production of carbon nanotubes, it was determined according to the toxicity caused by exposure to harmful chemicals during each process. The analysis of the security in the synthesis of carbon nanotubes process is determined by Eq(9) - Eq(13), where the safety for each technology is a function of the variables of the process defined in the optimisation of the synthesis process.

$$Saf = f_t^{Saf}(V_U) \tag{9}$$

$$f_t^{Saff} = R^{Carbonsource} + R^{Catalyst} + R^{gas} \tag{10}$$

$$R^{Carbonsource} = f(m_{Carbonsource})) \frac{0.5}{LD_{50}^{CS} M} \tag{11}$$

$$R^{Catalyst} = f(m_{Catalyst})) \frac{0.5}{LD_{50}^{C} M} \tag{12}$$

$$R^{Gas} = f(m_{gas})) \frac{0.5}{LD_{50}^{GI} M} \tag{13}$$

The LD_{50} values were obtained from the database of the software SCRI (SCRI 2013) and the considered average weight of an adult (w) was 70 kg.
Table 4 shows the correlation for carbon source and solvent as function of process parameters for each technology.

Table 4: Toxicity Correlations for each technology

Technology	Correlation for carbon source	Correlation for solvent
Arc discharge	$v_1 = 10.9 + 7.7 \bullet v_2 - 0.008 \bullet v_3 - 0.0015 \bullet v_4 + 0.103 \bullet v_5$	$v_2 = -1.42 + 0.115 \bullet v_1 + 0.0099 \bullet v_3 + 0.00089 \bullet v_4 - 0.0082 \bullet v_5$
Laser ablation	$v_1 = 0.32 + 5.06 \bullet v_2 + 0.002 \bullet v_3 - 0.032 \bullet v_4 + 0.24 \bullet v_5$	$v_2 = -0.304 + 0.027 \bullet v_1 + 0.00027 \bullet v_3 + 0.00055 \bullet v_4 + 0.0024 \bullet v_5$
CVD camphor	$v_1 = 4.42 - 2.351 \bullet v_2 + 0.0029 \bullet v_3 - 0.123 \bullet v_4 + 0.086 \bullet v_5$	$v_2 = 0.237 - 0.03 \bullet v_1 + 0.00032 \bullet v_3 - 0.0081 \bullet v_4 + 0.005 \bullet v_5$
CVD turpentine	$v_1 = -2.005 + 0.19 \bullet v_2 - 0.000055 \bullet v_3 + 0.04 \bullet v_4 + 0.29 \bullet v_5$	$v_2 = -0.239 + 0.0025 \bullet v_1 + 0.00028 \bullet v_3 + 0.0015 \bullet v_4 + 0.0094 \bullet v_5$

2. Results and discussion

2.1 Optimisation for efficiency and costs.

The correlations obtained in Statgraphics and the equations for determining the cost were coded in the software GAMS (Brooke et al., 2015). The problem consists of 26 variables, 35 constraints and 3 binary variables and it is solved in 0.16 s of CPU time in a computer with an Intel processor at 2.4 GHz with 8 GB of RAM. The results are shown in Table 5, it should be noticed that the best economic solution involves the use of CVD using turpentine as carbon source; whereas the use of camphor as carbon source in CVD provides a solution with a moderate cost but with the minimum efficiency. Arc discharge and laser ablation yield the worst economic scenario with a moderate efficiency. For a further analysis, Figure 2 shows a comparison for the different technologies and the obtained costs, where the relationships between the cost and the efficiency for the technologies studied in this paper are shown. It should be noted that the minimum cost with the maximum efficiency is for the CVD with turpentine as carbon source. Notice in Figure 2 that for the arc discharge method the cost per gram of carbon nanotubes increases from zero with 0 % efficiency to 18.645 USD at ~100 % efficiency. With respect to the laser ablation method, the cost increases from zero at 0 % of efficiency to 14.438 USD at ~100 % efficiency. While for the chemical vapour deposition method, the cost increases from zero to 3.419 at ~100 % efficiency when camphor is used as carbon source, and it increases from zero to 0.374 USD at ~100 % efficiency when the turpentine is used as carbon source.

2.2 Toxicity determination.

The toxicity results for the different optimal solutions are shown graphically in Figure 3. Notice that the damage for the arc discharge method caused by exposition to the carbon source is too small due to the occasioned damage associated to the catalyst is 0.002 % of fatalities for exposure to 0.050 g during 5 min. For the laser ablation method the used catalyst represents 0.225 % of fatalities caused for exposure to 0.001 g during 1 min. With respect to the CVD method, using camphor as carbon source, it represents 0.001656 % of fatality caused for the exposure to 0.004 g of catalyst during 12 min and 0.01945 % fatalities for exposure to 0.100 g of carbon source during 12 min. Finally, for the CVD method using turpentine as carbon source, a value of 0.00088 % fatalities for exposure to 0.1 g of catalyst during 8 min and 0.000006 % of fatalities for exposure to 4 g of carbon source during 8 min were observed. Therefore, from the safety point of view, the safest technology is the one associated to the CVD method using turpentine as carbon source and ferrocene as catalyst. Notice that for the arc discharge and laser ablation methods the exposure value of the carbon source is small and so it is represented as N/A.

Table 5: Optimal results

Technology	Cost (USD/g)	Efficiency (%)
Arc discharge	15.6528	1
Laser ablation	13.4163	12
CVD camphor	1.3030	1
CVD turpentine	0.3713	97

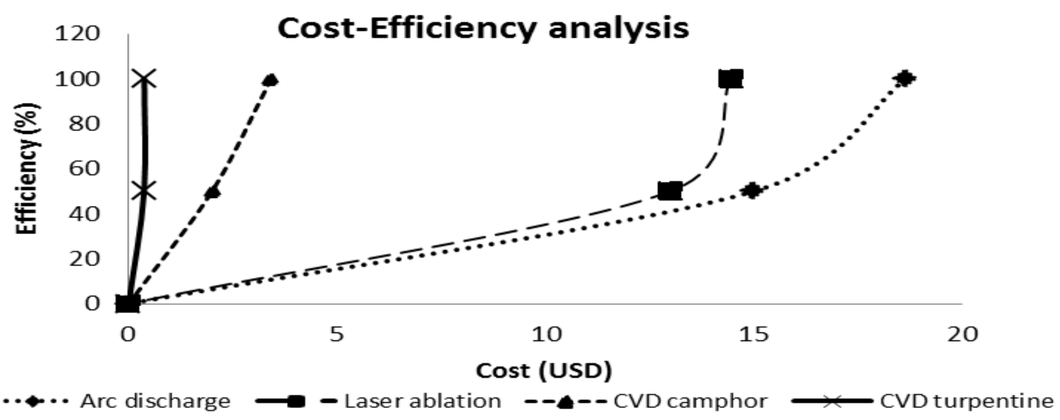

Figure 2: Results for cost and efficiency for the evaluated technologies.

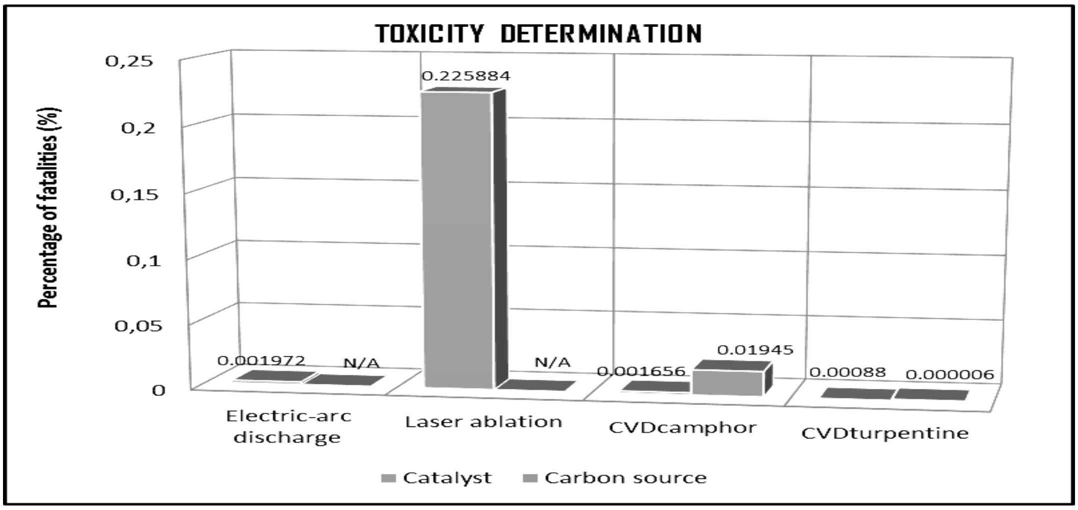

Figure 3: Percentage of fatalities for each method of synthesis of CNTs.

3. Conclusion

This paper has proposed a set of relationships to determine the best technology for synthesising carbon nanotubes considering three options of synthesis: arc discharge, laser ablation and chemical vapour deposition as a function of some independent variables involved in the different processes (i.e. carbon source weight, catalyst weight, temperature, gas flow, time, production cost and safety of the process); these relationships are integrated into a disjunctive programming formulation to determine the optimal conditions to yield the desired efficiency and the safest process at the minimum cost. A case study is presented, where, the safest technology with the minimum cost and maximum efficiency was the CVD using turpentine as carbon source, followed by CVD using camphor as carbon source. The laser ablation method represents the worst scenario with respect to safety and the arc ablation laser method is the worst solution with respect to the cost and efficiency. The proposed model was applied to a case study where the advantages of the proposed approach are highlighted. This approach can be useful to determine the minimum cost, maximum safety and operating conditions to yield a desirable maximum efficiency. Finally, the proposed approach is general and it can be easily extended to analyse other technologies for the synthesis of carbon nanotubes and different parameters.

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