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Article *in* Carbon letters · February 2020 DOI: 10.1007/s42823-020-00127-z



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Carbon Letters

ISSN 1976-4251

Carbon Lett. DOI 10.1007/s42823-020-00127-z





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ORIGINAL ARTICLE



Carbon precursor analysis for catalytic growth of carbon nanotube in flame synthesis based on semi-empirical approach

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Received: 10 November 2019 / Revised: 25 January 2020 / Accepted: 30 January 2020 @ Korean Carbon Society 2020

Abstract

Although flame synthesis promises economic benefit and rapid synthesis of carbon nanotube (CNT), the lack of control and understanding of the effects of flame parameters (e.g., temperature and precursor composition) impose some challenges in modelling and identifying CNT growth region for obtaining better throughput. The present study presents an investigation on the types of carbon precursor that affect CNT growth region on nickel catalyst particles in an ethylene inverse diffusion flame. An established CNT growth rate model that describes physical growth of CNT is utilised to predict CNT length and growth region using empirical inputs of flame temperature and species composition from the literature. Two variations of the model are employed to determine the dominant precursor for CNT growth which are the constant adsorption activation energy (CAAE) model and the varying adsorption activation energy (VAAE) model. The carbon precursors investigated include ethylene, acetylene, and carbon monoxide as base precursors and all possible combinations of the base precursors. In the CAAE model, the activation energy for adsorption of carbon precursor species on catalyst surface $E_{a,1}$ is held constant whereas in the VAAE model, $E_{a,1}$ is varied based on the investigated precursor. The sensitivity of the growth rate model is demonstrated by comparing the shifting of predicted growth regions between the CAAE model and the VAAE model where the CAAE model serves as a control case. Midpoint-based and threshold-based techniques are employed within each model to quantify the predicted CNT growth region. Growth region prediction based on the midpoint-VAAE approach demonstrates the importance of acetylene and carbon monoxide to some extent towards CNT growth. Ultimately, the threshold-VAAE model shows that the dominant precursor for CNT growth is the mixture of acetylene and carbon monoxide. A simplified reaction mechanism is proposed to describe the surface chemistry for precursor reactions with nickel catalyst where decomposition of the ethylene fuel source into acetylene and carbon monoxide is accounted for by chemisorption.

Keywords Carbon nanotube (CNT) · Modelling · Catalytic growth · Flame synthesis · Carbon precursor

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1 Introduction

Flame synthesis has been a subject of study that has been widely explored for synthesising various carbon nanomaterials including carbon nanotube (CNT) [1–3]. The fascinating mechanical, electrical, and thermal properties of CNT make CNT desirable for various fields of engineering and medical applications [4–6]. Carbon precursor is one of the key components for synthesizing CNTs alongside heat source and catalyst medium. However, the exact species that contributes towards CNT growth in flames with different fuel and temperature ranges remains unclear. In comparison to catalytic growth in homogeneous systems like chemical vapour deposition (CVD), the complexity in determining the key precursor in flames is more eminent where the species

composition and temperature distribution are naturally nonhomogeneous. Nonetheless, it is widely believed that both hydrocarbon in C_nH_m form and carbon monoxide are key growth precursors in flame synthesis of CNTs [7].

Various studies have emphasised that carbon monoxide is the precursor for CNT growth in flames. Flame synthesis studies in an engine environment where dodecane and ferrocene were employed as the fuel and the catalyst, respectively, show a positive correlation between carbon monoxide composition and CNT formation [8–10]. Vander Wal [11] reported that carbon monoxide is the favourable precursor for CNT growth using premixed flames in flame synthesis. In the same study, acetylene was found to be unfavourable for CNT growth as it contributes to catalyst deactivation [11]. Arana et al. pointed out that at high temperature, catalytic disassociation of carbon monoxide is more favourable [12]. The importance of carbon monoxide for CNT growth in flames has been reviewed elsewhere [13].

Other studies suggest that light hydrocarbons also contribute to CNT growth along with carbon monoxide. A review of flame synthesis studies by Mittal et al. suggests that acetylene C_2H_2 and carbon monoxide are the leading precursors in flame synthesis [14]. The said claim is supported by a flame synthesis experiment that suggested acetylene and carbon monoxide as the possible precursors in an ethylene inverse diffusion flame by combining the species composition, temperature, and CNT growth region within a flame structure analysis [15]. Since the carbon precursor was determined based on the product species, the contribution of ethylene as reactant towards CNT growth remains inconclusive. Another study claimed the important role of acetylene and carbon monoxide towards the formation of CNTs in inverse diffusion flames though the reported data on species composition shows that higher concentration of methane is found at the CNT growth region compared to acetylene and carbon monoxide [16]. In the studies of references [15, 16], the active carbon precursor was determined based on the species abundance in the region of CNT growth without considering the element of temperature in catalytic growth. Xu et al. mapped the growth region of CNTs that were synthesised in methane inverse diffusion flame via various catalysts in alloy form [17]. The study showed an abundance of ethylene and carbon monoxide at the region of CNT growth within multiple locations of the flame but the analysis of species contribution towards CNT growth was absent [17]. Although carbon monoxide is the active precursor in synthesizing CNT using nickel catalyst and ethylene in premixed flames, light hydrocarbons such as methane and acetylene were discovered contributing towards CNT growth too [18]. A linear relationship between methane and acetylene concentration with CNT mean diameter clearly indicates the great potential of both hydrocarbons as precursors [18].

Several CNT growth rate models have been developed to study catalytic growth of CNTs in CVD [19-24] and flames [25–28]. Puretzky et al. proposed a growth rate model in the form of kinetic equations that explain CNT growth processes and the interaction of carbon atoms with a catalyst particle [19]. Naha and Puri [20] adopted a previously developed diamond nucleation model [29] and integrated the model with the catalyst deactivation process in [19] to calculate CNT length and growth rate. The accuracy of the diamond nucleation model was later improved by Zainal et al. [30] via modification of the surface chemistry term of the model. Saeidi and Vaezzadeh [21] proposed a CNT growth rate model based on a phonon vibration model where CNT-catalyst interaction is assumed to be analogous to a mass-spring system. The phonon vibration model was further refined by the inclusion of catalyst deactivation parameter [24]. Zahed et al. [22, 23] adapted a correlation for thin film deposition to calculate CNT growth rate in CVD reactors, but the physics required to describe CNT growth processes is found lacking. It is noted that growth rate models for flame synthesis applications are rather scarce. Previously, the diamond nucleation model was employed to model CNT growth in flames by adapting parameters such as carbon diffusivity [25], flame temperature [27], and species composition [26, 28]. Due to limited experimental data for validation of CNT length and growth rate, validation works are often done based on CVD studies [25, 26, 28].

Modelling studies have also been carried out to analyse species distribution within the CNT growth region. A modelling study on the flame synthesis of CNT in methane diffusion flames predicted CNT length and growth region by assuming methane as the carbon precursor [28]. The study employed temperature and species composition obtained from computational fluid dynamics (CFD) as inputs to a growth rate model. Due to lack of prediction accuracies in temperature and combustion species, the size of growth region was overpredicted. The assumption of a single carbon precursor contributing to the CNT growth resulted in inaccurate representation in high-temperature gradient environment [28]. Another study used a three-step CNT growth model to demonstrate that carbon monoxide is the main precursor for the growth of single-walled CNTs in methane premixed flames [31]. Both temperature and species composition from a CFD simulation were post-processed using a stochastic particle method to determine the CNT growth [31]. Earlier modelling works by Naha and Puri [25] on CNT synthesis in ethylene diffusion flames suggested carbon monoxide and carbon dioxide as the dominant precursors for carbon deposition on iron catalyst particles. Unrau et al. [32] synthesised CNTs from ferrocene catalyst in an ethylene inverse diffusion flame and provided a general conclusion on the carbon precursor that contributes to the growth based on the predicted particles trajectory and

carbon precursor distribution with no growth rate model included. A recent study employed a multi-scale model to predict CNT growth region in inverse diffusion flames where the integration of detailed chemical kinetics within the CFD flame simulation was observed to yield accurate prediction of CNT growth region [28]. In the study, hydrocarbon fuel was assumed as the main precursor and prediction of CNT growth region was carried out based on a fixed adsorption activation energy [28].

The present study aims at predicting the CNT growth region using an established growth rate model with semiempirical approach where the measured species and temperature distribution from a published flame synthesis experiment is employed as model input. The prediction of CNT growth rate is done based on the precursor species concentration, local temperature, and residence time. Detailed analysis of the dominant carbon precursor(s) that contributes to the CNT growth at different temperature range is done at various regions within the flame. The contribution of specific precursors on CNT growth region is then discussed in the light of a proposed surface reaction.

2 Modelling

2.1 Growth rate model

The present study predicts CNT growth region based on a recent flame synthesis experiment of Padilla et al. who synthesised CNTs using nickel catalyst in an inverse diffusion flame setup [15]. Ethylene, benzene, and the mixture of both hydrocarbons were employed as the fuel source where CNTs were observed to grow only in the ethylene and ethylene-benzene flame [15]. Ethylene was chosen as the fuel in the present study due to the simpler hydrocarbon structure. A CNT growth rate model that has been previously developed [30] is employed in the present study.

The main equation of the model that describes the time evolution of the surface density of solid carbon atoms on the surface of a catalyst particle n_1 is shown by Eq. (1). The terms on the right-hand side of Eq. (1) describes the physical CNT growth processes due to interactions between carbon atoms and a catalyst particle. The number of carbon atoms remaining on the surface of a catalyst particle for a given time is related to the total amount of carbon that impinges on the particle N_{des} , the amount of carbon that undergo bulk diffusion through the catalyst particle N_{bd} , the amount of carbon that undergo bulk diffusion through the catalyst particle N_{sc} and critical clusters N_{cc} , and the amount of carbon that is converted into amorphous carbon layers N_{acl} .

$$\frac{dn_1}{dt} = N_{ad} - N_{des} - N_{bd} - N_{sc} - N_{cc} - N_{acl}.$$
 (1)

The adsorption term, N_{ad} represents the first physical interaction between carbon atoms and metal catalyst particle in the CNT growth process. The term N_{ad} captures the species composition including the type of carbon precursor which is defined by Eq. (2). Variable p_1 is the pre-exponential factor, whereas variable $E_{a,1}$ represents the activation energy for precursor adsorption on nickel catalyst particle surface. The term $F_{\rm b1}$ represents the flux of the carbon precursor molecules as described by Eq. (3). The catalyst surface area S_0 is determined based on a spherical geometry where the radius of the catalyst particle is 5 nm assuming growth of single-walled CNTs. Variables m and n are the mass and the partial density of the carbon precursor molecule, respectively. Partial density in Eq. (3) is calculated based on the measured mole fraction of carbon precursors from reference [15].

$$N_{\rm ad} = F_{\rm b1} p_1 \exp\left(-\frac{E_{\rm a,1}}{k_{\rm B}T}\right) \tag{2}$$

$$F_{\rm b1} = \frac{1}{4} S_0 n \left(\frac{k_{\rm B}T}{2\pi m}\right)^{\frac{1}{2}}.$$
 (3)

While some of the carbon atoms adsorb on the catalyst surface, those that do not adsorb undergo desorption away from the catalyst particle. The desorption term N_{des} in Eq. (1) can be expressed by Eq. (4) where variables τ_{res} and $E_{a,2}$ are the residence time of the adsorbed hydrocarbon before being desorbed away from the catalyst particle and the desorption activation energy, respectively. Constants v, and $k_{\rm B}$ denote the surface vibrational frequency of adsorbed species, and Boltzmann's constant, respectively. The responses of adsorption term in Eq. (2) and desorption term in Eq. (4) towards an identical value of activation energy are opposite to each other due to the sign difference in the exponential term of both the equations. The temperature T in Eq. (4) as well as in other terms within the growth rate model is based on the empirical data of ethylene inverse diffusion flame in [15].

$$N_{\rm des} = \frac{n_1}{\tau_{\rm res}} = \frac{1}{\nu} \exp\left(\frac{E_{\rm a,2}}{k_{\rm B}T}\right) \tag{4}$$

$$N_{\rm bd} = R_{\rm d,out} \big|_{t=t_{\rm s}} = C_0 \sqrt{\frac{D_{\rm b}}{\pi t}}.$$
(5)

Adsorbed carbon atoms experience bulk diffusion through the catalyst particle as modelled by the bulk diffusion term N_{bd} shown in Eq. (5). The rate of carbon diffusion out of the catalyst $R_{d,out}$ is evaluated at the saturation time t_s where the surface of a catalyst particle is saturated with carbon atoms. C_0 represents the volume concentration of carbon atoms at the surface of the catalyst particle, whereas $D_{\rm b}$ is the carbon bulk diffusivity which varies with the type of catalyst used. A constant $D_{\rm b}$ value of $1.36 \times 10^{-17} \,{\rm m}^2/{\rm s}$ is employed in the present study which corresponds to bulk diffusivity of carbon in nickel metal [30]. Carbon atoms that diffuse through the catalyst particle form two types of carbon clusters which are the critical cluster and the stable cluster. The critical cluster as represented by the term N_{cc} in Eq. (6) experiences decomposition into single atoms and contributes towards CNT growth. The critical threshold of carbon atoms is 10 before the critical cluster transforms into a stable cluster [33]. On the other hand, the stable cluster as represented by the term N_{sc} in Eq. (7) does not decompose into single carbon atoms and further agglomeration of this type of cluster would cause deactivation of the catalyst particle [20].

$$N_{\rm cc} = (i+1)\sigma_i D_{\rm s} n_1 n_i \tag{6}$$

$$N_{\rm sc} = \sigma_x D_s n_1 n_x. \tag{7}$$

Variables *i*, and σ_i in Eq. (6) represent the number of carbon atoms in a stable cluster and the capture number for a stable nuclei, respectively, whereas σ_x in Eq. (7) is the capture number of a critical nuclei. The surface diffusivity of carbon in a metal catalyst particle D_s varies with the type of catalyst and is taken to be 5.2×10^{-21} m²/s based on a previous study that models catalytic growth of CNTs on nickel [28]. Another physical process involved throughout the catalytic CNT growth is the formation of amorphous carbonaceous layer that encapsulates the catalyst surface and gradually deactivates the CNT growth site. This process is modelled by the last term in Eq. (1) N_{acl} which is described by Eq. (8).

$$N_{\rm acl} = \phi_{c1} \left(\frac{n_{p1} + n_{p2}}{\alpha_m n_m A_{np}} \right). \tag{8}$$

Based on Eq. (8), variables ϕ_{c1} , n_{p1} , n_{p2} , α_m , n_m , and A_{np} are the rate constant for catalyst deactivation, the concentration of carbonaceous layer, the concentration of inactive catalyst particles, the number of carbon monolayers, the surface density of carbon monolayers, and the surface area of catalyst nanoparticle, respectively. The entire growth rate model consists of a system of ordinary differential equation (ODE). For example, the surface density of critical clusters n_i and the surface density of stable clusters n_x in Eqs. (6) and (7), respectively, are dependent variables of two ODE functions. However, for the sake of brevity, only the major equations are shown here. Detailed explanation of the growth rate model can be found in reference [30]. The dependent variable n_1 that is solved from the main ODE in Eq. (1) is used to calculate CNT length using Eq. (9) where constants a_c and C^* are the diameter of a carbon atom and the amount of carbon required to form a monolayer, respectively.

$$L = \left[\frac{1}{a_{\rm c}C^*}\sqrt{\frac{D_{\rm b}}{\pi}}\right] \times \int_0^t \frac{n_1}{\sqrt{t}} {\rm d}t.$$
⁽⁹⁾

2.2 Prediction of CNT growth region

The growth rate model predicts CNT growth region based on the space of high CNT length which qualitatively represents the actual CNT growth region as observed from scanning electron microscopy (SEM) images. The plot of predicted CNT length via Eq. (9) is translated into CNT growth region based on the midpoint and the threshold method. In the former approach, the peak of the length plot is considered as the midpoint of the predicted growth region where the width of the predicted growth region follows that of the experiment. The latter method takes a range of CNT length that corresponds to a certain percentage of the peak of the length plot to be considered as the predicted CNT growth region. In the present study, the CNT length and growth region are determined using a total of seven precursors as listed in Table 1. The precursors include C₂H₄ (Case 1), C₂H₄ (Case 2), CO (Case 3), the combination of C_2H_4 and CO (Case 4), the combination of C₂H₂ and CO (Case 5), the combination of C_2H_4 and C_2H_2 (Case 6), and the combination of C_2H_4 , C_2H_2 , and CO (Case 7).

In the present study, two growth rate models are implemented based on constant adsorption activation energy (CAAE) and varying adsorption activation energy (VAAE), respectively. In the CAAE model, the adsorption activation energy $E_{a,1}$ in Eq. (2) is considered to be constant and takes the value of 600 kJ/mol based on a previous study that models surface chemistry of methane–ethylene fuel mixture with nickel catalyst [28]. On the other hand, the activation energy for precursor desorption $E_{a,2}$ in Equation (4) is varied. The $E_{a,2}$ values of single precursors (Cases 1–3) are varied based on Table 2, whereas the $E_{a,2}$ values of mixed precursor (Cases 4–7) are calculated using the mixing rule shown in Eq. (10) [34]. The CAAE model is physically less accurate as the surface chemistry between different precursor

Table 1 Prediction	of CNT
growth region based	1 on single
precursor and comb	ination of
multiple precursors	

Model	Precursor
Case 1	C ₂ H ₄
Case 2	C_2H_2
Case 3	CO
Case 4	C ₂ H ₄ CO
Case 5	C_2H_2 –CO
Case 6	$C_2H_4-C_2H_2$
Case 7	C ₂ H ₄ C ₂ H ₂ CO

 Table 2
 Activation energy for carbon precursor adsorption on nickel catalyst for base precursors

Precursor	$E_{a,1}$ (kJ/mol)		$E_{a,2}$ (kJ/mol)	
	CAAE	VAAE	CAAE	VAAE
C ₂ H ₄	600 [28]	203 [35]	203 [35]	203 [35]
C_2H_2	600 [<mark>28</mark>]	264 [35]	264 [35]	264 [<mark>35</mark>]
СО	600 [<mark>28</mark>]	106 [<mark>36</mark>]	106 [<mark>36</mark>]	106 [<mark>36</mark>]



Fig. 1 Schematic representation of the growth region locations. Flame image reprinted from [15]

and nickel metal happens at different rate. Nonetheless, the CAAE model is treated as a control study to investigate the sensitivity of the growth region prediction when $E_{a,2}$ is varied in isolation from the variation of $E_{a,1}$. In the VAAE model, both $E_{a,1}$ and $E_{a,2}$ are varied according to Table 2.

$$E_{\rm a,mix} = \sum_{i} \chi_i E_{\rm a,i}.$$
 (10)

3 Results and discussion

3.1 Midpoint-based prediction of CNT growth region

CNT growth region is predicted at height above the burner (HAB) of 0 mm, 15 mm, and 25 mm which represents the flame base, side, and tip, respectively, as shown in Fig. 1. CNT length plots are generated for each HAB where E_a

values from Table 2 (for Cases 1–3) and calculated $E_{a,mix}$ values from Eq. (10) (for Cases 4–7) are substituted into both Eqs. (4) and (2). The resulting CNT length plots calculated in Eq. (9) are shown in Fig. 2. CNT lengths are first predicted based on the CAAE model using individual and combined precursors as shown in Fig. 2a, c, e and b, d, and f respectively. The normalised CNT length represents the CNT length predicted by case $n L_n$ divided by the maximum CNT length predicted by the same case $L_{max,n}$ where the subscript *n* denotes the case number. The radial distance is normalised with respect to the burner radius R=10 mm. Based on Fig. 2, the black shaded band represents the experimental CNT growth region, whereas the peaks of the line plots underneath the black band are the high CNT growth region predicted by various precursors.

By just observing the line plots in Fig. 2, it is noted that the peaks of the predicted CNT length for most of the cases lie within close proximity with the experimental one. A preliminary observation on Fig. 2a, b would suggest Case 1 (C_2H_4) and Case 7 $(C_2H_4-C_2H_2-CO)$ as the potential precursors for CNT growth at 0 mm HAB. It is apparent that none of the single precursor prediction provides close prediction of CNT growth region at 15 mm HAB as shown in Fig. 2c. Nevertheless, the location of maximum CNT length lies quite close to the centre of the growth region measured in the experiment based on Fig. 2d for mixed species in both Case 5 (C_2H_2 -CO) and Case 6 (C_2H_4 - C_2H_2). As shown in Fig. 2e, carbon monoxide is seen to be a dominant precursor at 25 mm HAB, whereas the CNT length prediction based on ethylene and acetylene at the same HAB shows a reducing trend towards the centreline.

A flame structure approach is devised to link the precursor prediction with the growth temperature and species measurements [15] as shown in Fig. 3. Temperature and species mole fraction are plotted on the left and the right axis, respectively, over the radial length of the burner. The actual CNT growth region is again represented by the black band. Gray bands from top to bottom represent the predicted CNT growth region based on different precursor(s) from Case 1 to 7. The predicted CNT growth region of each band is determined with midpoint-based prediction that takes the peak of predicted CNT length in Fig. 2 and extends the growth region from the peak to the left and the right-hand side according to half-width of the experimental growth region. The said technique indicates that the accuracy of the predicted growth region solely depends on the accuracy of maximum CNT length location.

Figure 3 shows prediction of the growth region using the CAAE model (Fig. 3a, c and e) and the VAAE model (Fig. 3b, d and f) with their respective measured thermochemical properties of the gas phase from reference [15]. Here, the CAAE model serves as a control study to observe the response of the predicted growth region when the

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Fig. 2 Comparison between predicted CNT length plot and experimental growth region based on individual and combined precursors using the CAAE model at **a**, **b** 0 mm HAB, **c**, **d** 15 mm HAB, and

adsorption activation energies $E_{a,1}$ and $E_{a,2}$ are varied. There are noticeable shifts in predicted growth region at all HAB when different models are employed which indicates high sensitivity of the growth rate model. A general comparison between the panels at the left and the right in Fig. 3 shows a consistent trend of predicted CNT growth region being shifted to the left when the model changes from CAAE to VAAE. At 0 mm HAB, it is noted that Case 3 is highly sensitive towards the activation energy variation compared to other cases as observed from Figs. 3a and 4a. Considering the left boundary of the predicted growth region as an indicator, a 40% shift is estimated for Case 3 at 0 mm HAB

e, f 25 mm HAB. The black band represents CNT growth region reported by reference [15]

based on a 4 mm change in position of the left boundary. At 15 mm HAB, all of the predicted growth regions experience more than 15% shift towards the left with the exception of Case 7 as the model changes from CAAE to VAAE as shown in Fig. 3c, d. At similar HAB, Case 3 shows the highest sensitivity compared to the rest of the cases with a shift of approximately 60%. Significant change in growth region prediction is also observed for all cases at 25 mm HAB in Figs. 3e and 4e where the estimated shifting all of the cases are well over 20%. Based on Fig. 3b, d and f for the midpoint-VAAE model, it is observed that Case 1 (C_2H_4), Case 6 (C_2H_4 - C_2H_2), and Case 3 (CO) are the dominant



Fig. 3 Prediction of CNT growth region using the midpoint technique based on the CAAE model at **a** 0 mm HAB, **c** 15 mm HAB, and **e** and based on the VAAE model at **b** 0 mm HAB, **d**, **f** 25 mm HAB

precursors at 0 mm HAB, 15 mm HAB, and 25 mm HAB respectively. The listed dominant precursor shows the importance of C_2H_2 and CO though only to some extent.

3.2 Threshold-based prediction of CNT growth region

The prediction of CNT growth region using the threshold technique is based on SEM observation of CNTs. A specific threshold value is set to separate dense and sparse CNT growth within a predicted growth region. To find the optimised threshold value, a sensitivity analysis is carried out at 80%, 70%, and 60% of the maximum length of the individual length plots in Fig. 2. The optimised threshold value is 70%.

Accordingly, the CNT growth regions are predicted based on this threshold value for both CAAE and VAAE models as shown in Fig. 4.

Based on Fig. 4a, c and e, Case 2 (C_2H_2) is the dominant precursor at 0 mm HAB and 15 mm HAB, whereas Case 3 (CO) is the dominant precursor at 25 mm HAB when the CAAE model is employed. A similar trend is shown in a recent study where fuel hydrocarbon was identified as the dominant precursor at 4 mm HAB and 12 mm HAB of an inverse diffusion flame though the study was not extended to locations further downstream of the flame [28]. The study employed the same multi-scale model where 80–90% accuracy of growth region prediction is achieved when the CAAE-threshold technique is

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Fig. 4 Prediction of CNT growth region using the threshold technique based on the CAAE model at **a** 0 mm HAB, **c** 15 mm HAB, and **e** and 25 mm HAB based on the VAAE model at **b** 0 mm HAB, **d** 15 mm HAB, and **f** 25 mm HAB

employed [28]. Using the VAAE model, the mixture of C_2H_2 -CO (Case 5) is seen as the dominant precursor for CNT growth at all flame heights as shown by Fig. 4b, d and f. In fact, both C_2H_2 and CO, whether they appear standalone or combined, have been observed as the dominant precursors. This finding agrees with another study which reported that high concentration of acetylene and carbon monoxide are found to overlap with the catalyst trajectory at downstream locations of the flame [32], suggesting that both precursors experience the most interaction with the catalyst particles prior to CNT formation.

There are multiple predicted growth regions that fully overlap with the experimental growth region e.g., Cases 4, 5, 6, and 7 as evident in Fig. 4d. However, majority of the said cases tend to overpredict the experimental growth region which is a form of inaccuracy. In the previous study, a threshold of no CNT growth was introduced to curb the overprediction in which the growth region is truncated at the tails of the length plot [28]. However, the same method could not be applied here since the tails of the length plots in Fig. 2 do not consistently touch the horizontal axis. For this reason, a no-overlap criterion is introduced to filter out cases that significantly predicts CNT growth but simultaneously exhibits overprediction. A bar chart is presented in Fig. 5, comparing percentages of overlapping and non-overlapping



Fig. 5 Comparison of percentage of CNT growth region for Cases 1-7 that overlaps and does not overlap with the experimental growth region at **a** 0 mm HAB, (**b**) 15 mm HAB, and **c** 25 mm HAB based on the threshold technique and the VAAE model

between predicted and experimental growth regions in Fig. 4a-f.

Based on Fig. 5, the overlap bars are generated based on the percentage of the width of experimental growth region that is predicted by a case. On the other hand, the no-overlap bars are produced by taking the percentage of predicted growth region that does not overlap with the experimental one. It can be observed that Case 5 consistently shows the highest overlapping percentage across all HABs with 95%,

 Table 3
 Summary of dominant precursors based on the VAAE model

HAB (mm)	Midpoint method	Threshold method
0 (base)	Case 1 (C_2H_4)	Case 5 (C_2H_2 -CO)
15 (side)	Case 6 (C_2H_4 - C_2H_2)	Case 5 (C_2H_2 -CO)
25 (tip)	Case 3 (CO)	Case 5 (C_2H_2 -CO)

100%, and 100% overlapping in Fig. 5a–c, respectively. For non-overlapping data, Case 5 is found as the second best after Case 2 at 0 mm HAB (Fig. 5a), second best after Case 1 at 15 mm HAB (Fig. 5b), and second best after the cases without the non-overlapping bars at 25 mm HAB in Fig. 5c. On the basis of Case 5, it is evident that the growth prediction with varying adsorption and desorption energies coupled with threshold-based identification of CNT growth region reveals that C_2H_2 –CO is the dominant precursor for CNT growth.

Using the experimental growth region as the indicator, the actual temperature range for CNT growth is approximately 800 K–1200 K, 950 K–1400 K, and 1050 K–1450 K for flame heights of 0 mm, 15 mm, and 25 mm, respectively. These high-temperature ranges at all flame locations clearly indicate favourable catalytic decomposition, chemisorption of ethylene fuel and adsorption rate of combustion products like carbon monoxide at the surface of a nickel catalyst particle. Similarly, in a different study, dissociation of carbon monoxide was found favourable at high temperature with the presence of nickel catalyst [12]. The identification of C_2H_2 as one of the dominant precursors alongside carbon monoxide finally solves some earlier hypothesis discussed in [15]. In the study, C_2H_2 and CO concentration were observed to coincide with the actual growth region.

Table 3 summarizes findings of the best predicted dominant precursors based on the midpoint and the threshold methods. Regardless of the methods used, CO is the dominant precursor at the flame tip either in singular form (Case 3) or combined form (Case 5). Similarly, C_2H_2 is also a dominant precursor at the flame base and flame side (Cases 5 and 6); in exception of Case 1 at 0 mm HAB using the midpoint-VAAE model. Despite the crude assumption of the midpoint-based technique and the oversimplified physics of the CAAE model, the predictions of C₂H₂ and CO as dominant precursors are largely consistent with the methods adopted, as demonstrated in Table 3. In a nutshell, the fact that C_2H_2 and CO dominates other species in predicting CNT growth region for all methods (see Table 3) conforms the earlier claim that C₂H₂ and CO are the leading precursors for CNT growth in flame synthesis previously reported in [14].

Having concluded that Case 5 (C_2H_2 –CO) is the dominant precursor for the ethylene inverse diffusion flame, a reaction mechanism is proposed as shown in Table 4. Considering the

 Table 4
 Proposed reaction mechanism for precursor contribution to CNT growth

Proposed reaction	$E_{\rm a}$ (kJ/mol)	<i>T</i> (K)
	139 (base)	800-1200
$2C_2H_4 + 2.5O_2$	187 (side)	900-1400
$\rightarrow C_2H_2 + 2CO + 3H_2O$	190 (tip)	1050– 1450

high temperature throughout the entire CNT growth region, it is suggested that the adsorption mechanism responsible for the CNT growth process is chemisorption. The double bond structure of C_2H_4 changes into a triple bond C_2H_2 structure while the hydrogen atoms have dissociated. Furthermore, other C_2H_4 molecules are completely disintegrated from the fuel and forms new compounds with other elements such as oxygen to form CO.

4 Conclusion

A CNT growth rate model was employed in the present study to investigate the type of carbon precursor that contributes to CNT growth region in ethylene inverse diffusion flames. Data on flame temperature and species composition from a previous flame synthesis experiment were used as inputs to the growth rate model. The prediction of CNT length and growth region was carried out using ethylene, acetylene, carbon monoxide, and all possible combinations of two to three species as precursors. The growth region prediction was done at the base, side, and tip of the flame which corresponds to 0 mm HAB, 15 mm HAB, and 25 mm HAB, respectively. Midpoint-based and threshold-based methods of quantifying the predicted CNT growth region was carried out and compared. The effects of precursor type on the CNT growth region were simulated by manipulating the adsorption activation energy $E_{a,1}$ where a constant $E_{a,1}$ and varying $E_{a,1}$ represents the CAAE and the VAAE model, respectively. Prior to that, a control study is carried out by comparing the change in growth region between the CAAE model and the VAAE model. The control study shows the growth rate model is highly sensitive towards the change in activation energy with most cases at all HABs showing at least 15% shift in growth region. The threshold-based approach combined with varying activation energy was chosen as the method to determine the dominant precursor due to its appropriate surface chemistry. The accuracy of predicted growth region was presented via overlapping percentage with the actual growth region. Based on the threshold-VAAE model, C₂H₂-CO is identified as the dominant precursor at all flame heights under study. A reaction mechanism for precursor contribution towards CNT growth

was proposed where the contribution of C_2H_2 and CO is largely by chemisorption.

Acknowledgements This research was supported by Ministry of Education (MOE) through Fundamental Research Grant Scheme (FRGS/1/2019/TK05/UTM/02/8) with cost centre numbers R.J130000.7851.5F182 and Universiti Teknologi Malaysia (UTM) through UTM Fundamental Research (UTMFR: PY/2019/01657) grant with cost centre number Q.J130000.2551.21H10.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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