Chemical kinetics modelling for the effect of chimney on diffusion flame in carbon nanotubes synthesis

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Abstract. Hydrocarbon flame syntheses of carbon nanotubes (CNTs) on various metals substrates have been reported in literature, but existing methods are limited to usage of high melting temperature metals substrate due to excessive temperature in conventional diffusion flame burner. To address this limitation, high thermal conductivity chimney is innovatively incorporated into the diffusion burner to control flame temperature. Hence, the aim of this study is to investigate the effect of chimney application on the interaction behaviour between flame temperature profile and concentration of post combustion species distribution of diffusion flame. In this study, Computational Fluids Dynamics (CFD) – Chemical Kinetics (Chemkin) coupling method is used to simulate the flow and transport behaviour of laminar methane-air mixture in combustion environment. Kinetics mechanism is imported into species transport model of Chemkin simulator to further determine the reaction between combustion species and temperature profile of the mixture. Heat transfer models are then integrated into simulation to investigate the cooling effect of chimney during the combustion of methane-air mixture. This numerical simulation study provides insights on effects of chimney application towards cooling, species concentration, flame temperature and paving path for controlling the growth of CNT on low melting temperature metal substrate. Numerical models show improvement in temperature controls, increase in gas species concentration and in surface area that is favourable for growth of CNTs.

1 Introduction

Benefits of flame synthesis in growing CNTs have gained attention since its discovery. Releasing both heat and carbon source via combustion and pyrolysis, hydrocarbon provides an alternative cheap energy source for growing CNTs growth on metal substrates [1-2]. Synthesis of CNTs in different burners have been covered on premixed flame burner [1], normal diffusion flame (NDF) burner [2] and inverse diffusion flame (IDF) burner [3]. Optimum conditions for growing CNTs were characterised on each burner configuration with different type of metal catalyst and hydrocarbon fuel [2-4]. Based on initial characterisation established on the optimum condition in growing CNTs on each type of burner, recent developments on flame synthesis have expanded towards optimisation of burner designs in order to improve yields and qualities of CNTs such as development of flame assisted chemical vapour deposition hybrid burner [5], improvement on reactant gas tube position on premixed flame [6], application of water [7] and sulphur as additives [5]. Despite recent optimisations on burner designs, high temperature environment in flame synthesis limits the application of synthesizing CNTs on low melting temperature metal substrate. Inspired from application of chimney on premixed flame [4] that allows better controls of temperature, this paper would like to addresses the gaps presence in controlling temperature on IDF via the application of numerical simulation with the aid of high thermal conductivity chimney. Gas species in post combustion regions, temperature range that could promote nucleation and growth of CNTs would be identified in this paper.

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2 Numerical Modelling

2.1 Numerical model configuration, domain and boundary conditions

As this paper investigation is carried out based on co-annular IDF of Wu et al [8], the computational domain, Fig. 1, consists two-dimensional model of 70mm length by 28mm width. Linear velocity of air, 0.315m/s is introduced at oxidiser inlet while linear velocity of methane, 0.1076m/s is introduced at fuel inlet. Chimney application in the numerical models is positioned at 10mm above inlets with the length of 20mm and thickness of 2mm. Stainless-steel is considered as materials for chimney due to its relatively high melting point and thermal conductivity property. Numerical computation would be carried out without chimney to validate numerical model with the comparison of experimental data by Wu et al [8]. Temperature profile obtained from numerical model is in agreement with experimental data. After validation, numerical computation with inclusion of chimney application would be carried out. Numerical computations are executed on Ansys 2021R1 Fluent. A steady-state, laminar flow, asymmetric and segregated algorithm approaches are employed in computing these numerical models. Pressure based SimpleC solver is used to solve CFD component while stiff chemistry solver is used to solve chemical kinetics reactions. Interaction between CFD – Chemkin is carried out by stiff chemistry solver. After each CFD flow iterations, stiff chemistry solver will update all chemical reactions within the boundary region. At low laminar velocity flow of gas species mixture, flame structure is greatly affected by buoyancy forces, gravity is considered in current study in order obtain more accurate prediction in flame structure. Combustion reaction code, Grimech 3.0 which describes 325 reactions and 53 species [9] is applied into Chemkin simulator. Chemical kinetics reactions in laminar flow consider only Arrhenius rate as its finite rate kinetic computation. As for thermodynamics predictions of gas species, thermal conductivity and viscosity of gas species components are calculated based on ideal gas mixing law. Specific heat capacity of respective gas species components is calculated based on mixing law. CFD interaction with chimney is defined by no slip flow boundary condition. System coupled heat transfer is used to simulate heat flux transfer from near flame region to external environment of chimney wall structure which is in contrast to heat sink models [4]. For species radiation absorption models, discrete ordinates radiation model is chosen for better prediction outcome on natural gas such as methane with weighted-sum-of-gray-gases model domain-based consideration. A cold flow with only oxygen (O$_2$), methane (CH$_4$), nitrogen (N$_2$) species is computed primarily in the domain with convergence criteria of 10$^{-6}$ on energy and 10$^{-3}$ on continuity and flow [10]. Once cold flow convergence is achieved, high temperature of 1700K is introduced to near inlet region to initiate combustion chemical reaction. Volumetric chemical reaction is activated with inclusion of multispecies diffusion options. All 53 species and discrete ordinate-intensity equations are activated in the second set of calculation with inclusion of chemical reaction.

Fig. 1. Computational domain of numerical investigation on inverse diffusion flame burner.
3 Results and discussions

3.1 Models’ validation

As noted in flame synthesis of CNTs via IDF [3], CNTs were grown on substrate at yellow flame region situated above blue flame region. According to experimental data from Wu [8], the height of blue flame axis was at 15.8mm height. Hence radial temperature validations of numerical model against experimental data [8] are carried out at flame height of 18.1mm, 24.1mm and 33.2mm. Burner inlet plane as illustrated in Figure 1 is defined as origin of height. Validation model is simulated without chimney and it has the same set-up condition as experimental data [8]. This validation process would provide references for results obtained by numerical models in incorporations of chimneys at section 3.2. As observed in Fig. 2, overall trendlines and predictions in regards to exterior of flame front region are in agreement with experimental data [8] with a margin of around 200K. Increases in flame height reduces the difference in peak temperature between numerical models and experimental data [8]. Gradient of temperature decreased faster towards exterior in radial direction as compared to experimental data.

Fig. 2. Radial distribution of temperature profile at heights of (a) 18.1mm, (b) 24.1mm and (c) 33.2mm above burner inlet between validation models and experimental data from Wu [8].

Fig. 3. Validation of numerical models on gas species concentration with Wu [8] experimental data for CO, CO$_2$, and H$_2$.

Overall trendlines on evolutions of gas species, Fig. 3, are in agreement with experimental data. Under prediction of carbon monoxide (CO) and carbon dioxide (CO$_2$) compared to experimental data with correction factor of 2 times for CO at peak concentration from height of 20mm onwards and 1.5 times for CO$_2$ at peak concentration at height of 17mm. Correction factor maintained at 1.3 times for CO$_2$ from 20mm height onwards. Under prediction of CO are in agreement with numerical results of normal diffusion flame from Mokhov [11] on methane/air combustion which is considered at the range of 40%.
3.2 Application of chimney

Syntheses of CNTs were reported to occur at a wide range of temperature from 800K – 1600K [2-5, 12]. Present methods on synthesis of CNTs via IDF and NDF would require substrates to undergo high temperature environment which exceeds 1250K temperature. Growths of CNTs in IDF were limited to outer boundary of yellow flame region where part of substrate was exposed to yellow flame region with temperature of more than 1250K [3]. Application of chimney is expected to enable investigations on growth of CNTs on working temperature lower than 1250K which would be suitable for low melting point substrate such as anodic aluminium oxide template, gold, silver and copper.

The placement of chimney of 20mm length and 2mm thick is at radius ranging from 6mm to 8mm with 0.5mm increment. The controlled temperature seek via chimney application is between 800K to 1250K at yellow flame region. In flame synthesis, pyrolysis of CH$_4$ in rich fuel mixture occurs at yellow flame region. In this region, CH$_4$ is broken down into CO and acetylene (C$_2$H$_2$) carbon precursors that are responsible for growth of CNTs. Vander wal [13] suggested that dissociative adsorption of carbon precursors onto catalyst particles starts via Boudouard reaction at temperature range of 800K – 1000K. Once carbon concentration reached sufficient level to induce formation of carbide on metal catalyst particles, hydrogenation reaction would contribute to deposition of carbon precursor to catalyst surface in addition of Boudouard reaction. Another route was proposed via deposition of pyrolyzed hydrocarbon onto substrate surface is believed to provide carbon source to adsorb onto surface of catalyst metal particles [2, 14]. Partial pressure of gas species is believed to affect the adsorption and diffusion of carbon precursors onto catalyst particles [14] due to potential difference in carbon precursors concentration.

Fig. 4 shows radial temperature distribution with application of chimney at the height of (a) 33.2mm and (b) 40mm. The black dotted lines in Figure 4 signify 800K and 1250K. CNTs growth is favourable within this temperature boundary. By using chimney radius as parameter, this paper aimed to achieve temperature control at this range. Significant increases in temperature across radial position could be observed across all radii. Steeper decreased in temperature with higher temperature range near flame axis are observed in smaller radius chimney of 6mm and 6.5mm while slower gradient decreased in temperature are observed in chimney with 8mm radius. At 40 mm height, it is observed that chimney with 8mm radius has increased the region where temperature range of 800K – 1250K by 1mm as compared to validation model without chimney application which translated to increase in 20% in radial distance. An increased in radial position from 5.2mm to 6.5mm is observed at 33.2mm height with chimney of 8mm radius. A further analysis is carried out on the influences of chimney application on surface areas that satisfy 800K – 1250K. Figure 4 shows that chimney with 8mm is most optimum at controlling the temperature at the range of 800K – 1250K. At 33.2mm height, an improvement of surface area of 38.57% compared to validation model without chimney. Besides, there is an improvement of 33.14% improvement at 40mm height compared to validation model without chimney at 33.2mm height. This provides higher surface area with favourable temperature conditions in promoting the growth of CNTs.
Fig. 5. Radial distributions within chimney of (a) CO at 33.2mm, (b) CO at 40mm, (c) C$_2$H$_2$ at 33.2mm and (d) C$_2$H$_2$ at 40mm.

Consideration of CO, and C$_2$H$_2$ in current study are based on carbon source for the growth of CNTs as reported in literature [2, 7, 13]. There exists preferential catalytic reactivity of CO towards Fe catalyst particles [15] and of C$_2$H$_2$ towards Ni catalyst particles [1]. In Figure 5, increases in gas species concentration for CO and C$_2$H$_2$ are observed across all radius configurations at both 33.2mm and 40mm height. Similar to CO and C$_2$H$_2$ gas species, computational models with chimney application also show increases in hydrogen (H$_2$), and water vapour (H$_2$O) concentration at 33.2mm and 40mm as well. The increased in CO and C$_2$H$_2$ concentration would increase potential growth rate of region for carbon nanotubes as suggested that diffusion of carbon precursors onto catalyst particles might depends on gas species concentration [16]. However, increased in gas concentration could not be correlated directly with the radius of chimney. This is suspected due to interference of CH$_4$ distribution on chimney with smaller radius.

4 Conclusions

Among the sets of radius dimensions investigated, chimney with 8mm radius came up to be the most optimum parameter in controlling temperature at the range of 800K – 1250K at the height of 33.2mm above burner inlets to favour the formation of CNTs. Improvement in favourable condition in surface area of 38.57% could be achieved with chimney of 8mm radius. At 40 mm height, a slight reduction in improvement of favourable condition surface area to 33.14%. Application of chimney prevented further dispersion of gas species along radius direction that helped in increasing gas species concentration at downstream of flame front, at height of 33.2mm and 40mm.
Based on current study, a further optimisation on fuel inlets designs could be carried out in order to address partial escapes of CH$_4$ from chimney with small radius due to big difference between size of fuel inlets and chimney.

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