Synthesis of single-walled carbon nanotubes in oxy-fuel inverse diffusion flames with online diagnostics

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Abstract

A novel technique for synthesis of single-walled carbon nanotubes (SWNTs) in diffusion flames is presented, as is a diagnostic tool that can provide online information about nanotube size, number density, and purity. An inverse diffusion flame with a high stoichiometric mixture fraction \( Z_{st} \) is used to produce SWNTs with an average length of 1 \( \mu \text{m} \). The high \( Z_{st} \) flame allows nanotubes to be produced in a fuel-rich region that is void of soot and polycyclic aromatic hydrocarbons (PAH). In addition, by operating as an inverse diffusion flame the carbon nanotubes (CNTs) are not exposed to oxygen and thus, can be collected downstream. Consequently, this flame provides a potential approach to large-scale synthesis of pure SWNTs. In addition, a differential mobility analyzer (DMA) is employed as an online diagnostic tool. The DMA can distinguish between excess catalyst particles and CNTs due to the differences in their electrical mobilities. Thus, the presence of CNTs as well as their size, number density, and purity relative to excess catalyst particles can be identified from the size distribution of the aerosol sampled downstream of the flame. This tool allows for rapid identification of the effect of changing process variables on nanotube growth and thus, the production process can be quickly optimized.

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Keywords: Single-walled carbon nanotubes; Stoichiometric mixture fraction; Oxygen-enrichment; Differential mobility analyzer; Online diagnostics

1. Introduction

Single-wall carbon nanotubes (SWNTs) possess many unique properties [1] making them desirable for applications ranging from electronics to composite materials [2]. In particular, SWNT composite materials could be useful for a wide variety of building applications due to the high strength-to-weight ratio of single-walled carbon nanotubes. Although these composites have great potential, structural applications, such as aircraft, would require large quantities of SWNTs, and production costs are currently much too high for any such application to be economically feasible.
Production rates on the order of kg/h are needed to reduce this cost to an acceptable level.

Flame reactors are presently used in industry for production of materials such as carbon black at kg/h rates and low cost [3]. Carbon black is produced in a continuous process by utilizing a hydrocarbon diffusion flame. The fact that diffusion flames are used in industry to produce carbonaceous particles suggests that this type of flame may also provide an approach to large-scale production of carbon nanotubes. Carbon nanotubes (CNTs) are typically produced using gas phase (floating catalyst) or substrate (supported catalyst) methods. In terms of large-scale production, gas-phase processes have a significant advantage over those using substrates because they are continuous, not batch, processes. Carbon nanotubes have been produced in the gas phase by Height et al. [4] and Diener et al. [5] in premixed flames, by Merchan-Merchan et al. [6] in counterflow diffusion flames and by Vander Wal et al. [7] in a normal coflow diffusion flame. From a practical perspective, diffusion flames tend to be safer than premixed flames. In addition, diffusion flames provide a relatively large number of parameters that can be varied to “design” the flame environment to be conducive to CNT growth.

While diffusion flame synthesis has the potential to achieve high production rates for CNTs, there are a number of challenges. First, in a normal diffusion flame, after the CNTs are formed the flow field moves them into a hot, oxidizing environment where they can oxidize. Thus, the synthesized product cannot be collected externally from the flame. Second, in a typical hydrocarbon diffusion flame, polycyclic aromatic hydrocarbons (PAH) are formed and these molecules are known to deactivate (poison) the catalyst particles, thus arresting nanotube growth [7]. Furthermore, the soot that is formed can act as an impurity on synthesized CNTs. Inverse, high Zad diffusion flame synthesis provides an approach to overcoming both of these challenges and this approach is explored in this work. In the inverse configuration, the CNTs will not burn up because they move into a fuel-rich environment as they are formed. In addition, high Zad combustion yields flames that are visibly free of soot and low in PAH [8].

Progress in producing larger amounts of CNTs has further been limited by the current methods of CNT analysis because they are offline methods. Samples must be collected for each process condition and analyzed using tools such as transmission electron microscopy (TEM) or Raman spectroscopy. On the other hand, nanotube production depends on many variables. For flame synthesis these include: fuel, oxidizer, and precursor concentrations; temperatures; residence time; and fuel and precursor type. Due to the large number of process variables, optimization is not practical unless an online method of analyzing the particles can be developed. In this work, a method based on the differential mobility analyzer (DMA) is employed to obtain online information on the formation of CNTs, their size and purity.

2. SWNT synthesis in high Zad inverse diffusion flames

Vander Wal et al. [7] used a coflow diffusion flame burner with fuel (ethylene and acetylene) and cobaltocene flowing through the inner tube and air through the outer to form a normal diffusion flame that was capable of producing SWNTs. The fuel was diluted to decrease the amount of soot formation. In this type of configuration, synthesized nanotubes must be extracted from the flame because once formed, the flow field moves them into a hot, oxidizing environment where they would oxidize. To avoid this, an inverse flame configuration is used in this study so that after the nanotubes are formed they flow into a fuel-rich region. In this configuration, the oxidizer is introduced through the inner tube and the fuel through the outer. This configuration has been used with CNT growth on substrate-supported catalysts [9], but has not been used for aerosol synthesis of nanotubes.

In an inverse diffusion flame, as in the normal flame, PAH and soot are formed, which can inhibit nanotube growth. Figure 1a illustrates an undiluted inverse ethylene/air flame. The intense yellow-orange luminosity indicates that a large amount of soot is being formed. Soot formation can be reduced by fuel dilution. However, even when the fuel is diluted to the blow off limit (Fig. 1b), soot is clearly still present.

On the other hand, the completely blue, stable flame shown in Fig. 1c is the result of a combination of oxygen-enrichment and fuel dilution. In this flame, the formation of PAH and soot is...
strongly affected by changes in the flame structure [8,10–13]. Here, “flame structure” describes the relationship between the temperature and species distributions and is characterized by the stoichiometric mixture fraction [14] defined as

\[ Z_{st} = \left(1 + Y_{F,0} W_{O,0} / Y_{O,0} W_{F,F} \right)^{-1} \]  

where \( Y \) is the mass fraction, \( W \) is the molecular mass, and \( v \) is the stoichiometric coefficient. Subscripts \( F \) and \( O \) refer to the fuel stream and oxidizer stream, respectively. The undiluted ethylene/air flame in Fig. 1a has a low \( Z_{st} \) of 0.064. The flame in Fig. 1b has a fuel concentration of 21\% and thus, a higher value of \( Z_{st} \) at 0.26. The flame in Fig. 1c has a high \( Z_{st} \) of 0.78 due to an 8.1\% concentration of fuel and the use of pure oxygen.

The high \( Z_{st} \) flame in Fig. 1c has a higher adiabatic flame temperature than the diluted ethylene/air flame (Fig. 1b), thus it is more stable at a lower fuel concentration and can be made soot-free. A small amount of PAH may form in an efficient manner, online information is needed on an adjusted sphere diameter equal to \((1.5D^2/L)^{1/3}\) where \( D \) and \( L \) are the diameter and length of the nanotube, respectively. The shape factor and the adjusted sphere diameter are both dependent on orientation relative to the direction of flow. Thus, the electrical mobility of a nanotube is a function of its shape, orientation, diameter, length, and the number of charges carried by the nanotube. In any aerosol synthesis process, many of the catalyst particles will not produce nanotubes and therefore catalyst particles must be classified separately from nanotubes. The spherical catalyst particles and the nanotubes often have similar diameters and if they also carry a similar amount of charge, CNTs will have a lower mobility than the catalyst particles because their aspect ratios are much greater than unity. The difference in mobility translates to different DMA classification voltages for the two types of particles and thus, the formation of catalysts and CNTs can be identified with the DMA. This difference in classification voltage has been theoretically demonstrated by Unrau et al. [16] and has been observed experimentally in flow reactor synthesis of carbon nanotubes [17,18].

The amount of impurities present on the synthesized nanotubes can also be determined from the size distribution measured with the DMA. If both inactive catalyst particles and CNTs are present, the size distribution will likely be bimodal. The ratio of the two peaks can indicate the amount of catalyst impurities on the synthesized nanotubes. More catalyst impurities will exist on the CNTs if a large fraction of the catalyst particles do not produce a nanotube. Finally, the DMA can provide online information about the actual size of the CNTs. If the diameter in Eq. (2) is known (or can be estimated from, for example, the catalyst particle size distribution), the number of charges can be calculated in a simple way using the method developed by Unrau et al. [16]. Thus, by using a DMA and Eq. (2), a range of lengths can be estimated.

In this study, a high \( Z_{st} \) ethylene inverse diffusion flame was used to synthesize carbon nanotubes. Catalyst particles were produced in situ by introducing ferrocene with the fuel stream. A differential mobility analyzer coupled to a sampling probe was used to monitor the size distribution of the flame while varying the fuel concentration. Samples were size-selected using the DMA and subsequently collected for validation of the online size distribution results using transmission electron microscopy.

### 4. Experiment

An inverse diffusion flame of an enriched-oxidizer and diluted fuel was established on a coflow burner with concentric tubes of 8 and 51 mm diameter. Fuel, nitrogen, and ferrocene were introduced through the outer tube with flow rates given in Table 1. Ferrocene was chosen as the precursor primarily because of its favorable decomposition temperature. Ferrocene was introduced at a mass flow rate of 0.5 mg/min by flowing nitrogen through a bubbler filled with ferrocene powder. Oxygen and nitrogen were introduced through the inner tube. For all experiments the adiabatic flame temperature was maintained at 1920 K [10] and the flame height was maintained at 30 mm ± 1 mm. \( Z_{st} \) was varied from 0.69 to 0.85. Nitrogen was added to the oxidizer stream...
as the fuel concentration was increased to maintain the same adiabatic flame temperature. All flows were controlled using calibrated rotameters. Based on these calibrations, the concentrations presented in subsequent sections are accurate to within ±3%.

The flame was surrounded by a large plexiglass chimney to minimize disturbance. The aerosol was sampled with a quartz probe mounted vertically above the flame, and the probe tip was 3 cm from the flame to minimize its influence. The probe was connected to a scanning mobility particle sizer (SMPS) consisting of an impactor, a Kr 85 bipolar ion source, a TSI 3085 nano-DMA, a TSI 3025A condensation particle counter (CPC), and a PC to run the software. This system was used to monitor the size distribution of the aerosol as $Z_{st}$ was varied. The peak diameters and number concentrations in the size distributions presented were reproducible to within ±5%. Samples were collected directly on TEM grids by selecting a DMA voltage and collecting the resultant particle stream at the exit of the nano-DMA using a high-efficiency electrostatic sampler. The samples were analyzed using a high-resolution transmission electron microscope (HR-TEM).

5. Results

As stated in the previous section, $Z_{st}$ was varied between 0.69 and 0.85 while maintaining an adiabatic flame temperature of 1920 K. Under these high $Z_{st}$ conditions, the flames are free of soot in that they are pure blue with no visible yellow emission. These flames are far from their sooting limits. For example, for $Z_{st} = 0.78$ yellow emission is not observed until the adiabatic flame temperature is 2300 K, 400 °C greater than the adiabatic flame temperatures used in this study. A flame near the sooting limit will have a tendency to form more PAH, which would be detrimental to CNT growth.

The first operating condition was obtained by burning in pure oxygen and decreasing the fuel concentration until the flame was near the blow-off limit. This flame, flame A in Table 1, had a $Z_{st}$ of 0.85 and an adiabatic flame temperature ($T_{ad}$) of 1920 K. The size distribution measured by the DMA at these settings is shown in Fig. 2. This size distribution contains only one peak located at an equivalent mobility diameter of about 14 nm. The lack of a second peak in this distribution indicates that no significant amount of carbon nanotubes are being produced. The size distribution was also measured at these settings without the addition of ferrocene and no particles

<table>
<thead>
<tr>
<th>$Z_{st}$</th>
<th>Mole fraction of C$_2$H$_4$</th>
<th>Mole fraction of O$_2$</th>
<th>$m_{inner}$ (mg/s) ±3%</th>
<th>$m_{outer}$ (mg/s) ±3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame A</td>
<td>0.85</td>
<td>0.051</td>
<td>1.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Flame B</td>
<td>0.74</td>
<td>0.059</td>
<td>0.75</td>
<td>6.3</td>
</tr>
<tr>
<td>Flame C</td>
<td>0.69</td>
<td>0.063</td>
<td>0.45</td>
<td>7.4</td>
</tr>
</tbody>
</table>
were detected, indicating that the particles of Fig. 2 are either iron or iron oxide.

The fuel concentration was increased to 5.9% and the oxygen concentration was reduced to 75% producing flame B in Table 1 with a $Z_{st}$ of 0.74. The corresponding size distribution is shown in Fig. 3. This distribution is clearly bimodal with one peak at an equivalent mobility diameter of 8 nm and the other at 48 nm. The presence of the second peak and the large separation between the peaks provides a good indication that nanotubes or nanofibers are being produced. Each peak was size-selected using the DMA and a sample was collected for TEM analysis. For the sample collected at a DMA setting of 8 nm, only catalyst particles encapsulated by disordered carbon were observed (Fig. 4). A distribution of catalyst particle sizes is present, ranging from 2 nm to greater than 10 nm.

Figure 5a illustrates some typical single-walled carbon nanotubes observed from a sample collected at a DMA setting of 48 nm. Only SWNTs were observed and these nanotubes were generally straight with an average diameter of 2 nm and an average length of about 1 μm based on a sample size of 20 SWNTs. A coating of amorphous carbon and catalyst particles is observed on some parts of the tubes while other sections are clean. A higher magnification is shown in Fig. 5b, illustrating the lighter core of the tube relative to the walls. The walls of this tube were initially straight but were deformed by the electron beam of the TEM at high magnification.

Finally, flame C in Table 1 was produced with a $Z_{st}$ of 0.69 by increasing the fuel concentration to 6.3% and decreasing the oxygen concentration to 45%. The size distribution was measured with and without the addition of ferrocene to ensure that the particles were not soot and no particles were detected without the addition of ferrocene. The size distribution resulting from the addition of ferrocene is shown in Fig. 6. This distribution is still bimodal indicating some nanotube formation. The second peak is at the same location as that in Fig. 3, although the number density has been reduced by nearly two orders of magnitude. The first peak has shifted to about 6.5 nm, which is less than its location in either Figs. 2 or 3. In general, as fuel concentration is increased, the second peak corresponding to nanotube production appears and then disappears while the first peak shifts steadily to the left, corresponding to a smaller equivalent mobility diameter.

Size distributions were also determined for all flames using a long DMA to extend the measurement range out to an equivalent mobility diameter of 250 nm. No peaks were observed beyond 48 nm for any $Z_{st}$ and it is not likely that any would appear beyond 250 nm since this would correspond to SWNTs significantly longer than a few microns.

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![Fig. 4. TEM micrograph of encapsulated catalyst particles collected from flame B at a DMA setting of 8 nm.](image1)

![Fig. 5. TEM micrograph of (a) typical SWNTs observed from a sample collected from flame B at a DMA setting of 48 nm, (b) high magnification image showing the inner core of the nanotubes.](image2)
Fe$_2$O$_3$ would cause the size of the catalyst particle from Fe to FeO to increase. Assuming that the first peak for flame oxidation occurs for higher $Z_{st}$ combustion. Although amorphous carbon is present at some locations on the tubes, there is far less than that found in Ref. [7] in dilute-fuel/air diffusion flames. Using a different precursor such as iron pentacarbonyl may further reduce these impurities as noted by Vander Wal et al. [7]. A number of catalyst particles are also present as impurities on the synthesized SWNTs. These impurities can be decreased by introducing the ferrocene through a narrow region close to the

![Graph](image_url)

**Fig. 6.** Particle size distribution obtained from flame C at 3 cm above the flame tip.

6. Discussion

A comparison of Figs. 2, 3 and 6 demonstrates that SWNT formation only occurs in a narrow window of $Z_{st}$. Fuel concentration was varied only by 1.2% from flame A to flame C yet the change in the size distribution is dramatic. For a given temperature, an increase in fuel concentration might suggest that more carbon would be deposited on the catalyst particles, which would lead to a shift to a larger size. On the contrary, these figures show that the first peak of the distributions, which corresponds to catalyst particles encapsulated in disordered carbon, shifts to a smaller size for an increase in fuel concentration. In addition, the change in fuel concentration is small and thus, we do not anticipate that fuel concentration is the cause of the peak shift or the narrow window of SWNT formation.

One possible reason for the shift in the size distribution of the first peak is that when $Z_{st}$ is varied, there is a change in oxygen concentration in the high temperature zone and a shift in the location of the radical pool. As $Z_{st}$ is increased, the oxygen concentration in the high temperature zone increases [14], and the radical pool shifts towards the fuel side [19]. This combination of increasing oxygen concentration and a shift in the radical pool towards the fuel side with increasing $Z_{st}$ could influence the extent of oxidation of the iron catalyst particles, with greater oxidation occurring for higher $Z_{st}$. A transition of the catalyst particles from Fe to FeO to Fe$_2$O$_3$ would cause the size of the catalyst particles to increase. This increase would result in a shift in the first peak to the right as $Z_{st}$ is increased, which corresponds to what is observed. Assuming that the first peak for flame C (Fig. 6) corresponds to iron with a size of 6.5 nm, a transition to FeO would cause a size increase to 7.8 nm, which is close to the 8 nm diameter observed for flame B (Fig. 3). If the particles were further oxidized to Fe$_2$O$_3$, these particles would grow to 11 nm in diameter. This is reasonably close to the diameter of the first peak for flame A. Thus, oxidation of the particles may contribute to the trend of increasing catalyst particle size with increasing $Z_{st}$.

The change in oxygen concentration and the shift in the radical pool may also provide some explanation for the narrow window of SWNT formation with $Z_{st}$ because if the oxidation state and the size of the catalyst particle change, this could change the activity of the catalyst particle towards SWNT growth. Howard et al. [4] concluded that metal-oxides are the active catalyst for nanotube growth under flame conditions, which is consistent with the results of Yuan et al. [20] and Li et al. [21]. Furthermore, Dai et al. [22] have shown that formation of SWNTs requires catalysts of ~2 nm in size. Figures 3 and 6 clearly show that the size distributions of flames B and C both contain numerous particles of the appropriate size for SWNT formation (~2 nm). Nonetheless, flame B yields an order of magnitude more nanotubes that flame C. If, as suggested above, the catalyst particles of flame B consist of FeO, then a possible reason flame C produces less nanotubes is because Fe is less active than FeO, which agrees with the conclusions of Howard et al. [4].

As mentioned above, the diameter of the first peak of flame A (Fig. 2) may correspond to further oxidation of the catalyst particles to Fe$_2$O$_3$. Although this is a metal oxide, no nanotubes were observed for this flame. This can be understood by comparing Fig. 2 with Figs. 3 and 6. The particle concentration for sizes less that 4 nm in Fig. 2 is observed to be two orders of magnitudes less than those of flames B and C in Figs. 3 and 6. Thus, in this case it may be particle size, not particle composition, that is limiting nanotube growth.

The SWNTs produced in flame B had an average length of about 1 μm, which is the longest size known for gas phase diffusion flame synthesis of SWNTs. These nanotubes, shown in Fig. 5, clearly demonstrate the ability of a high $Z_{st}$ inverse diffusion flame to produce SWNTs at significant lengths. In addition, these nanotubes are relatively free of amorphous carbon impurities due to the use of high $Z_{st}$ combustion. Although amorphous carbon is present at some locations on the tubes, there is far less than that found in Ref. [7] in dilute-fuel/air diffusion flames.
flame instead of over the entire region of the outer flow. Some of the catalyst particles formed in the current configuration never pass through a region conducive to SWNT growth and thus, they only contribute to impurities.

The discovery of the narrow window for SWNT formation clearly demonstrates the capability of the DMA to provide useful online information about the CNT synthesis process. Without the DMA, this window would be extremely difficult to find. By measuring the size distribution with the DMA at each value of $Z_{st}$, the window of conditions suitable for SWNT formation was quickly identified as indicated by the appearance of the bimodal distribution in Fig. 3. In addition, the optimal condition for SWNT growth at this temperature, residence time, and ferrocene concentration was identified to be at a $Z_{st}$ of 0.79 and a $T_{ad}$ of 1920 K.

In addition to information about the formation of CNTs, Fig. 3 can also provide information about CNT size and purity. A comparison of this concentration to that of the first peak gives an estimate of the amount of catalyst impurities. A larger difference between the two peaks corresponds to a larger amount of catalyst impurities. Finally, an estimate of the actual size of the CNTs can be determined. The nanotubes were confirmed to be SWNTs by TEM analysis and the diameter was estimated to be about 2 nm. Using this diameter and the methodology outlined by Unrau et al. [16] assuming a charge of unity, an average length was estimated. This length was 0.8 μm, which is close to the average of 1 μm estimated from TEM analysis.

7. Conclusions

The capability of an inverse, high $Z_{st}$ diffusion flame to produce single-walled carbon nanotubes has been demonstrated. High $Z_{st}$ (oxy-fuel) combustion allows for production of nanotubes that contain fewer soot impurities than would be present if only fuel dilution was used. In addition, the inverse configuration allows the nanotubes to move into a fuel-rich environment after they form, as opposed to the oxidizing environment of a normal flame, allowing for external collection. Thus, the inverse, high $Z_{st}$ flame provides an excellent approach to large-scale CNT synthesis. The capability of a differential mobility analyzer to provide online CNT size distribution information has also been demonstrated. The DMA can distinguish between excess catalyst particles and carbon nanotubes and thus it can provide online information on CNT size, number density, and purity. This diagnostic tool allows the effect of changing process variables to be rapidly identified, thus providing a better understanding of nanotube formation and placing optimization of the production process on a practical timescale.

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