Synthesis of carbon nanotubes using fluidized bed technology

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Abstract—Current methods employed to synthesise carbon nanotubes (CNTs) include hot-wire chemical vapour deposition (CVD) techniques as well as laser ablation. These methods however produce small amounts of nanotubes at a high production cost. The use of a fluidized bed reactor was investigated for the synthesis of CNTs on a continuous basis, and in bulk. The main driver for the bulk production of CNTs lies within broadening the application range for CNTs.

The CSIR has successfully synthesised CNTs using virgin plastics as well as a carbonaceous gas using fluidized bed technology. Current investigations are underway to test various factors involved with the CNT growth and production. An understanding of these factors and their interactions could provide valuable information for producing CNTs in a fluidized bed process with the user's desired properties and characteristics.

INTRODUCTION

Many techniques have been employed to produce carbon nanotubes (CNTs). The most commonly used techniques include arc discharge, laser ablation, chemical vapour deposition (CVD) but they are generally aimed at producing Single Walled (SW) CNTs. Applications under research for SWCNTs include electronics (field emitters, transistors) and for catalyst support. However, a disadvantage of these techniques is that they produce very small amounts of CNTs, and therefore produce them at a very high cost.

In an attempt to produce CNTs on a larger scale (and thereby produce them at a lower cost), some researchers have investigated the use of a fluidized bed (FB), in order to benefit from the high gas/solids contact exhibited in an FB and to allow continuous operation. The goal of achieving higher production rates of Multi-Walled CNTs has been achieved. Most of the work is based on using as a bed material which is a prepared substrate impregnated with a catalyst (iron, nickel or cobalt, with iron being the most frequently used). The carbon source is a hydrocarbon gas such as ethylene or acetylene.

The CSIR became aware of the work of Umberto Arena (University of Naples) in 2005. In his work, he produced CNTs when pyrolysing plastics in a fluidized bed. The beauty of his work is that he uses silica sand or alumina as a bed material (without any surface treatment) and solid plastic as the carbon source. He achieved his best results (in terms of yield) from using Polyethylene Teraphthalate (PET), both virgin and recycled.

In preliminary test work aimed at reproducing Arena's results, nanostructures were successfully produced, with characterisation via Raman Spectroscopy showing conclusively the presence of carbon nanotubes. However, the group is not yet able to produce the nanotubes consistently and needs to gain more understanding of the effects of parameters including temperature, gas velocity, choice of support (bed) material etc. Also, one of the major problems experienced was the

formation of sinters/agglomerates resulting in defluidization inside the reactor which halted further production. In an attempt to minimise defluidization but yet understand the effect of each of these parameters, the CSIR has decided to simplify the process by replacing the polymer with a carbonaceous gas, i.e. ethylene. SEM images and Raman Spectroscopy has indicated that CNTs were successfully produced using ethylene and as such, a parametric study was thus undertaken and will be presented herein.

BACKGROUND

A number of novel technologies have been developed in an attempt to optimise the production of carbon nanotubes on a larger scale and with low overall costs. Amongst these technologies, investigations on the use of a fluidized bed pyrolyser have been employed to produce CNTs, namely spray pyrolysis without catalyst and the catalytic vapour deposition method have been reviewed. An initial review on the direct synthesis of multiwalled and single walled carbon nanotubes by spray-pyrolysis (Tapasztó et al, 2006) [9] showed that simultaneous synthesis of single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) by spray pyrolysis of ferrocene in benzene solution and in argon atmosphere showed best results for ferrocene concentration ~3g ferrocene in 50ml benzene, a flow rate of ferrocene-benzene solution of approximately 1ml/min and reaction tube temperature in the range 875-925°C. Promising results were observed in this method and displayed higher carbon efficiency than using the fluidized bed pyrolysis synthesis method.

Morancais, et al. (2006) [8] undertook a parametric study on the large scale production of multi-walled carbon nanotubes by fluidized bed catalytic chemical vapour deposition. In their studies, the effect of temperature, total pressure, and composition on the catalytic growth of multi-walled carbon nanotubes (MWCNT) was investigated. They concluded that temperature has a more pronounced effect on the morphology of the CNT hanks as well as the porosimetry properties of the MWCNTs. Other parameters had a less pronounced effect.

The core advantages of the FB-CCVD method were that experiments were fully reproducible because they led to high carbon conversions (more than 75%) and had an excellent selectivity in MWCNTs. The elutriation was also negligible, indicating that MWCNT remained anchored on the catalytic particles in the fluidized bed. This concept was also adapted by the CSIR research group, but it remained apparent that more experimental work and research has to be done to achieve best operating variables and a suitable type of bed material yielding an almost pure MWCNT product.

Maintaining the best operating parameters could improve quality and production of CNTs in this investigation. By understanding the effect that operating parameters have on the CNT growth mechanisms, a cost effective method can be proposed for large-scale continuous production of CNTs. Compared to other techniques (laser ablation and arc discharge methods) which produce CNTs on a small scale, CVD synthesis was identified as the better method for large-scale production (Thostenson et al., 2001, Goddard et al., 2002) [10]. It was also shown that other existing CNTs synthesis methods can only produce high-quality nanotubes in yields suitable for limited research use (Park et al., 2001, Joubert, et al., 1997).

Large scale production of carbon nanotubes in a nano-agglomerate fluidized-bed reactor (NAFBR) (Wang et al., 2002) [12] showed that carbon nanotubes produced by catalytic chemical vapour deposition (CCVD) can be formed into loose agglomerates that can be fluidized during the growth process. Comparing the CCVD method with laser ablation and arc discharge methods, shows it to be more economical due to the use of lower reaction temperatures and thus no need for special materials of construction.

To achieve the growth of CNTs in a NAFBR, the input flow of hydrogen is a crucial factor to reduce the rate of carbon soot production by dehydrogenation so that more ordered and thermodynamically stable MWCNTs can be produced. The role of hydrogen in the synthesis of CNTs was also investigated in the synthesis of CNTs by the CVD method (Wasel et al., 2000) [13]. In their experiments, they used xylene as a carbon source and ferrocene as a catalyst. The catalyst was introduced by a two-step method, either by dissolving in xylene or by placing the catalyst powder in the preheated zone to deposit iron catalyst particles on the reactor walls prior to introducing the pure xylene into reactor. Hydrogen was introduced at a constant flow and the effect on the production of soot and/or carbon fibres were studied. They concluded that there exists an optimal flow rate of

hydrogen depending on the carbon source used that could minimise soot formation and thus produce a much cleaner product.

The Arkema Research Centre in Lacq was one of the major companies to have launched projects aimed at the large scale production of multiwalled carbon nanotubes in their large scale laboratory pilot plant (Gaillard et al., 2006). They used a hydrocarbon gas such as ethylene as a carbon source, and an iron-based catalyst. MWCNTs were produced in a fluidized bed and the MWCNT bundles obtained were formulated in order to provide them with the desired properties. The process was optimised to achieve a process that was highly reproducible and a product of a very consistent nature. This highlights the significance of accurately controlling the operating parameters, since synthesis parameters are believed to the crucial factor in controlling the structure of the tube. Also the role of an efficient catalyst was demonstrated through achieving consistent MWCNTs production of 1 kg/h. The Arkema research group managed to produce graphite strength – MWCNTs having 10 -15 walls and an outside diameter around 12nm and apparent density between 50 -150 kg/m3. The product formed was highly entangled multi-walled nanotube bundles measuring several micrometers in length.
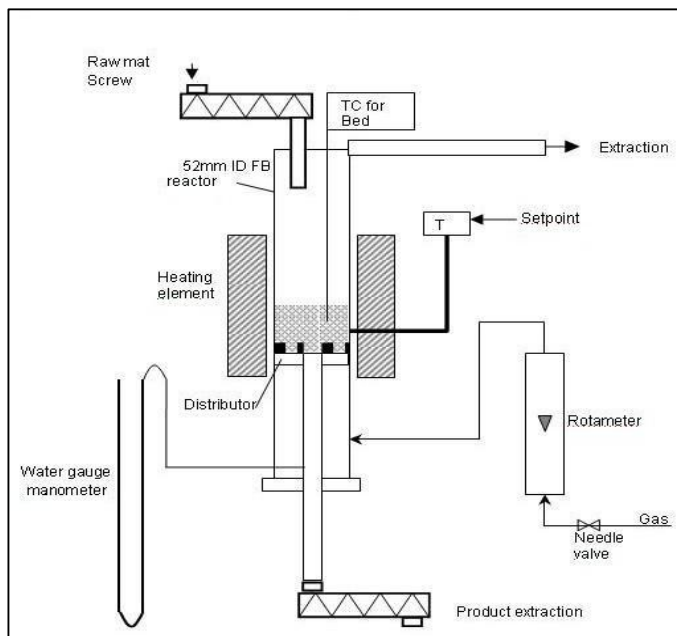
An innovative process for mass production of CNTs was proposed by Arena (2005). His work focussed on the production of multi-walled carbon nanotubes by means of pyrolysis of virgin polyolefins in a FB-CCVD operation. Unlike most other researchers and current methods, Arena used a solid-gas fluidized bed reactor, continuously operated under conditions which allowed high heating rates of the polymers, high heat and material exchange coefficients and reliable control of residence time in the reactor. Arena mentions that present methods, mostly reviewed above, utilize graphite, carbon monoxide or hydrocarbons for the construction of the carbon skeleton of CNT. His investigation takes into consideration the possibility of large scale production of CNTs at significantly lower costs due to the use of recycled plastics. Arena's work describes the first results on the production of multi-walled carbon nanotubes by means of fluidized bed pyrolysis of virgin or recycled polypropylene, of high quality similar to MWCNTs available in the market. Investigations were also done on the fluidized bed pyrolysis of polyethylene and that of the mixtures of polyolefins, with similar conditions to the initial report as previously mentioned. The product produced by the different plastics did not differ much, with just noticeable changes in yield obtained. He also reports that his best overall yield was obtained using PET as the feed material.

Various other researchers have also started to investigate the use of plastics as feedstock for synthesising CNTs (Yee-wen et al, 2007). In their work, they have also investigated the use of polycarbosilane (PCS). Similar to Arena's work, they synthesized CNTs by a novel method using chemical vapour deposition-fluidized bed reactor (CVD-FBR).

The key factor of a nano-agglomerate fluidized bed reactor is that heat and mass transfer is rapid, therefore maintaining the entire fluidized bed at the same temperature and reactant concentration. Ultimately, the operation could be controlled simply and reliably. All the work reviewed thus far looked at the synthesis of CNTs in fluidized bed pyrolysis. New literature has recently been found where investigators are looking into the combustion of polypropylene (Zhiwei et al, 2006) in the presence of a catalyst, specifically nickel compounds such as: Ni2O3, NiO, Ni (OH)2 and NiCO3. These compounds were used in the presence of organo-modified montmorillonite (OMMT) at 630 -830°C. This method displays a completely different view and operation than the pyrolysis method discussed above. The combustion process produced CNTs and the efficiency of this process, based on the critical observations on the proton acid sites from the degraded OMMT layers, played an important role in the catalytic degradation of PP to supply carbon sources that can be catalyzed by the nickel catalyst for growth of MWCNTs. From the review it was gathered that the combination of nickel compounds with OMMT was a key factor to efficiently synthesize MWCNTs via catalytic combustion of PP. This opens a new synthesis method not previously considered by the CSIR, as a fluidized bed reactor can easily be operated in either pyrolysis or combustion mode.

EXPERIMENTAL

The experimental setup, as shown in Figure 1, consisted of a 52 mm diameter fluidized bed (FB). Nitrogen and hydrogen (and ethylene in later experiments) were passed separately through rotameters and then to the distributor. The bed was externally heated via six electrical elements and the bed temperature was measured by means of a thermocouple. A "preheater" was also installed

prior to the gas mixture entering the distributor. A preheat temperature ranging between 60ºC and 150ºC was achieved in the bed prior to external heating, and dependent on the gas flow rate used. The pressure drop across the bed was measured by means of a manometer. Plastic and bed material was fed through the top of the FB, bed material was extracted from the bottom and elutriated fines were captured in a bubbler, situated at the back-end of the system.

Figure 1: Schematic representation of the fluidized bed reactor.

Scanning electron microscopy was used to image the as-produced samples. The samples were also analysed using Raman spectroscopy at a wavelength of 514nm over the range 0 – 3000cm-1.

RESULTS AND DISCUSSION

The first sets of results presented here were produced by using polymers as a feedstock. feed.
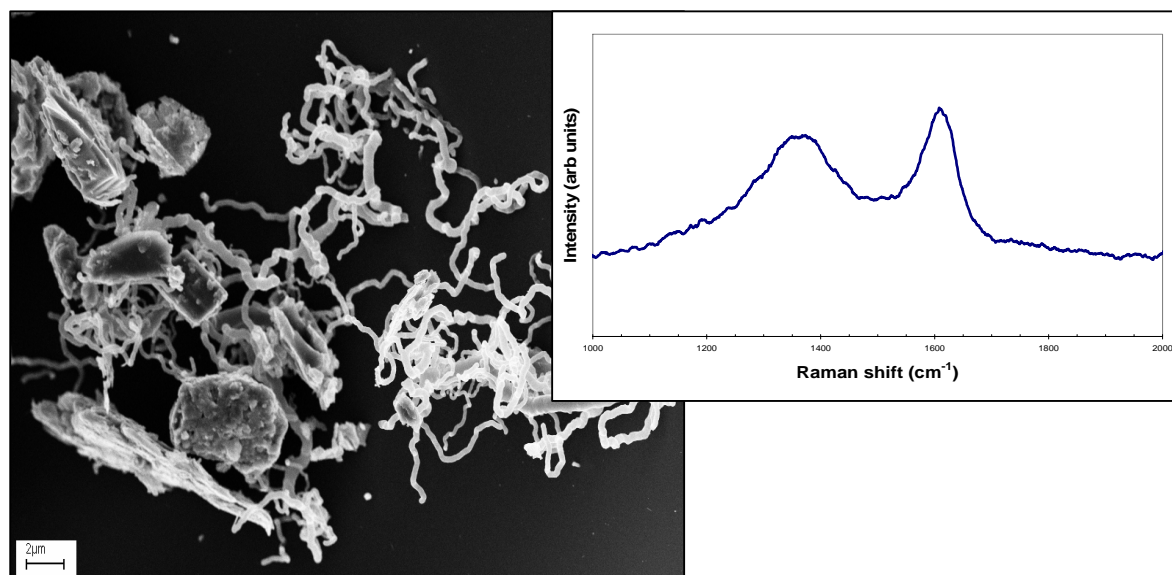
Figure 2: SEM and accompanying Raman Spectra of nanostructures produced on a silica support using PET as

Figure 2 shows structures with a high degree of buckling and are indicative of poor structured nanotubes. The diameters of these structures ranged between 200 nm and 400 nm. Analysis of the Raman spectra indicates structures with a high degree of impurities. The distinct double peaks on the Raman spectra are indicative for the formation of carbon nanotubes.

Two distinct peaks are noticed and this is indicative of carbon nanotubes formation. The lower peak (the D-band) relates to disorder or impurities in the sample. A broad D-band peak indicates many types of impurities, i.e. buckling, amorphous carbon and other structural defects. The higher peak (the G-band) relates to the graphitic vibration of the tubes, and this peak is usually situated at 1580cm-1. The ratio of the G/D bands is also usually used as an indication on the purity of the samples.

The impurities can be attributed to the methods of growth as proposed by Arena in his work. A polymer particle reaches its softening point when it is introduced into the bed. This allows the particle to melt over the bed particles and thus covers the bed materials with a layer of polymer. This was noted in the samples, but these SEM images are not presented here. From this polymer coating, the volatiles are released during the pyrolysis stage and together with the polymer degradation products, CNTs grow from the surface. Should the pyrolysis process not be efficient, the selectivity towards CNTs decreases. The result is bed particles coated with softened polymer which then tends to stick together. This results in sinter formation inside the bed.

Lots of nanostructures were identified in the sinters. The sinters formed were soft sinters that were easily broken by hand. When these sinters were analysed under SEM, the nanostructures were mostly noticed on the inside of the sinters. This indicates that the above premise still holds as the inside of a sinter would still be under pyrolysis conditions even though the rest of the sinter lies in the colder regions towards the extraction at the bottom of the reactor. Some of these structures are presented in Figure 3.
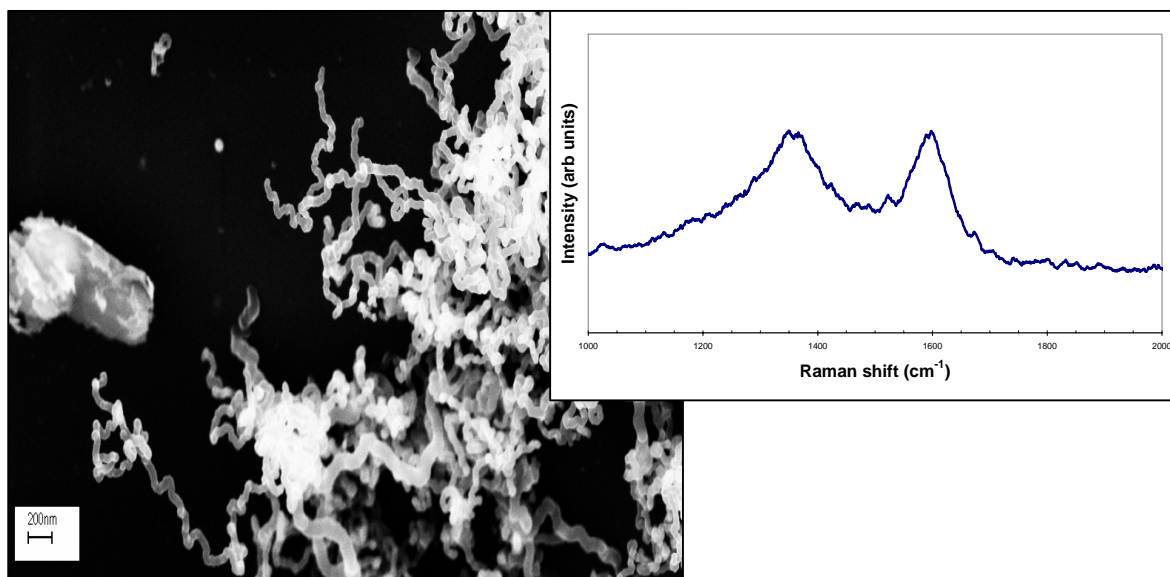

Figure 3: SEM and accompanying Raman Spectra of nanostructures observed in a sinter.

Also shown in Figures 2 and 3 are the Raman spectra for the samples. The Raman data also indicates the poor quality of the produced CNTs with a broad profile. The small ratio of the G/D bands also indicates the poor quality of CNTs produced.

Under further tested conditions, a sharper peak at 1580 cm-1 was noted, as seen in Figure 4. The diameters of these structures ranged between 100 nm and 200 nm, with lengths in the micron ranges. Under these conditions, looking at the SEM images as well, smoother structures were observed. Although the D-band is still present in the Raman spectra, this can be contributed to all the amorphous carbon structures as a result of the pyrolysis products. Further purification needs to be completed to reduce the D-band peak and thus increasing the G/D band ratio.

When comparing the Raman spectra of Figure 4 with those of Figure 2, the narrowing of the D-band is

immediately noticeable. This highlights the fact that nanotubes formed under these conditions are of a greater purity and contains fewer defects. This is observable in the smoother structures as seen in the SEM images.
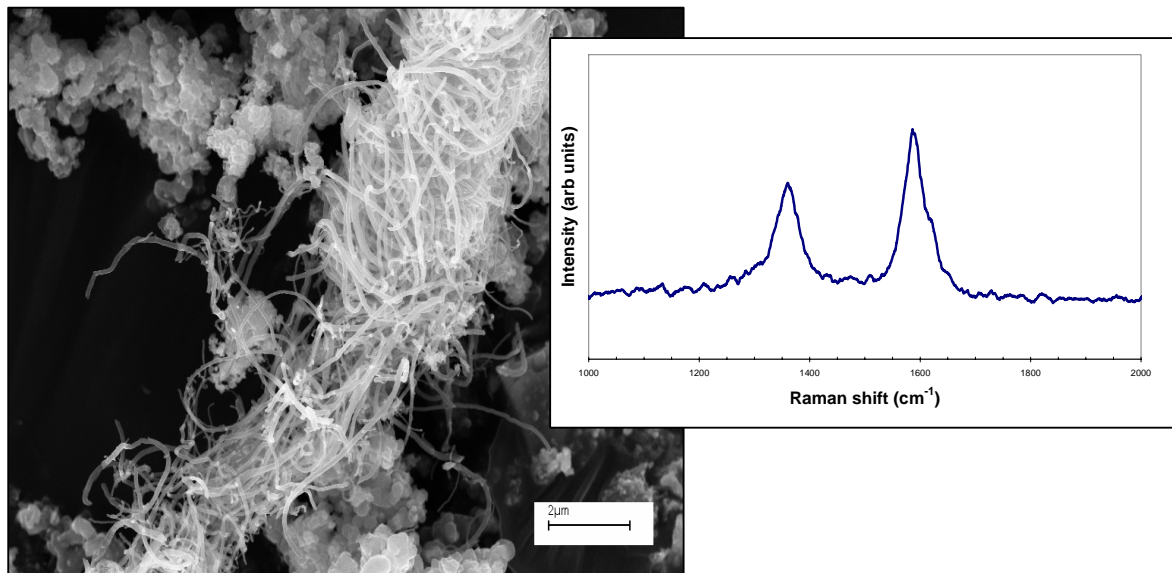

Figure 4: SEM and accompanying Raman Spectra of nanostructures produced on an alumina support using LDPE as feed.

The parametric study using a polymer feed could not be completed due to multiple operational issues related to the polymer feed. Although the defluidization could be overcome as suggested in literature, this phenomenon seemed more random during these experiments. To thus ensure repeatability for the experiments, it was decided to simplify feedstock so as to minimise the stoppages and thus increase repeatability.

When ethylene gas was used, more ordered and longer CNTs were produced as shown in Figure 5. The diameters of these structures ranged between 80 nm and 100 nm and lengths in the micron ranges. This results in nanotubes with very promising aspect ratios (length to diameter). Literature dictates that nanotubes with high aspect ratios are favoured as those CNTs have superior chemical and mechanical properties.

The use of ethylene eliminates the bed from defluidizing yet still provides enough data to determine the importance of various parameters for the growth of CNTs in a fluidized bed reactor.

Current studies are underway at the CSIR where a factorial design will be undertaken to determine the interactions of 9 independent variables identified during the FB operation process. It should be noted here why there are no calculations regarding the efficiency or the conversion of the process presented in this paper. This was largely due to the difficulty in the purification using this technique. Whereas Arena had reported harvesting most of his CNTs in the back-end of his process, it was found that the CNTs produced using the polymeric route, and supported in other literature, was anchored securely to the substrate material.
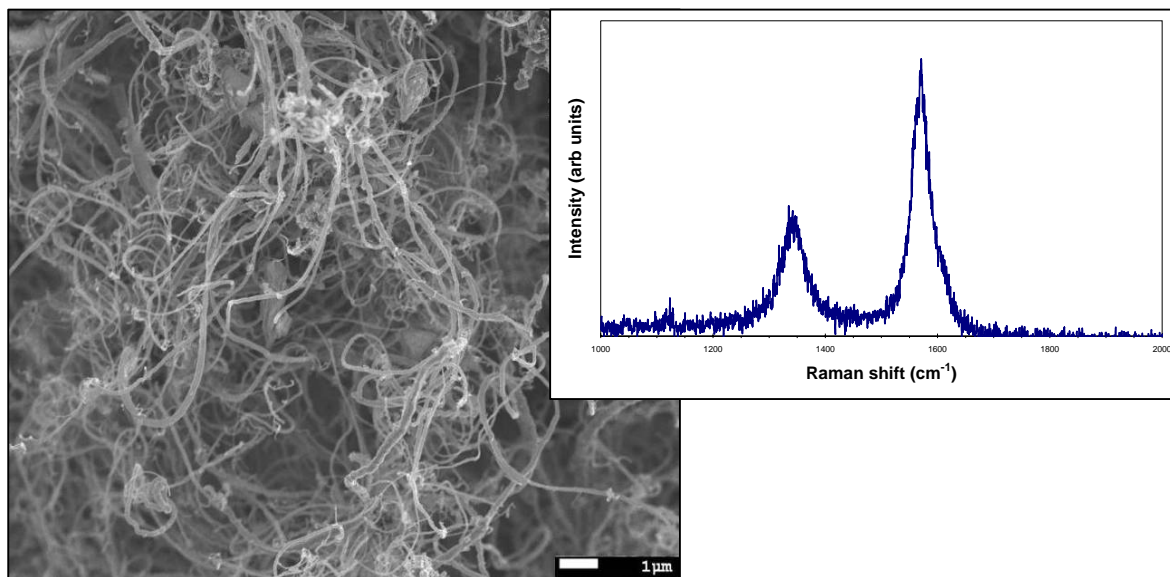
Figure 5: SEM and accompanying Raman Spectra of CNT produced using ethylene feedstock on alumina substrate.

Aggressive purification methods are thus required, which would make bulk production very hazardous. These methods are currently being evaluated at the CSIR.

CONCLUSIONS

The fluidized bed process provides an easy up scalable method for continuous, bulk synthesis of carbon nanotubes. It has been shown that CNTs can be produced using either a polymer or gaseous feed, but purification methods needs to be addressed in order to understand the effect of various parameters on the growth and conversion of CNTs.

Various CNT structures were reported herein and these could all be attributed to the operating conditions at which there nanotubes were synthesised. With this in mind, and getting an understanding of the parameters involved, CNTs can be produced according to users' specific requirements.

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