

## Fine Spray Generation for Single-Wall Carbon Nanotubes (SWCNT) Production

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### Abstract

Gas flaring is the burning of natural gas, which cannot be processed or sold during oil and gas production and processing operations. In past decades, gas flaring was believed to be environmentally tolerable. On the contrary the flaring of gas has been found to be an impediment to the environment; this has led to attempting to tackle the problem of gas flaring to advance it to an acceptable level worldwide.

There are currently over 700,000 gas wells worldwide and according to World Bank about 110 billion cubic meters (bcm) of natural gas are flared annually. If all the flared gas is stopped and instead converted to hydrogen (H<sub>2</sub>) and carbon (C) nanotubes, the reduction of CO<sub>2</sub> emissions which stands at 400 million metric tonnes per annum could be drastically reduced. The hydrogen component produced from the reaction could then be used for power generation and the irregular carbon nanotubes as composite materials.

The main aim of this investigation was to develop an alternative approach to continuous gas flaring in oil and gas industry. Sprays and atomisation techniques were experimentally employed as a promising option for the production of Single-Walled Carbon Nanotubes (SWCNT).

Laboratory experiments were performed to test the concept of using this technique to study the effects of the related parameters on its behaviour by spraying simulated catalyst solution (i.e. water) droplets into a hydrocarbon gas stream (methane as a carbon source) using a specially designed “atomiser device” that incorporates a number of pressure swirl atomisers.

A furnace was installed underneath of the “atomiser device” and the stream of droplet particles fell down through the furnace (400 - 800° C). Reactions which took place inside the furnace produced the Single-Wall Carbon Nanotubes (SWCNT) material from natural gas stream. The effect of water flow rate (0.001- 0.005 l/min) and water supply pressure ( $\leq 12$ MPa) as well as the gas flow rate (0.3-0.4 l/min) together with the down-stream distance of the corresponding atomiser device on the droplet size distribution ( $\leq 5\mu\text{m}$ ) were also characterised. The qualitative and quantitative analysis of the results obtained from the series of trials demonstrated that the production of SWCNT is certainly possible by using a combination of pressure swirl atomisers.

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### Introduction

Natural gas plays an important role in the energy needs of the world. It is mainly composed of methane but it is typically mixed with varying amounts of heavier hydrocarbons such as ethane, propane, butane and pentane [1]. In addition, raw natural gas contains water vapour, hydrogen sulphide, carbon dioxide, helium, nitrogen, and other compounds. Natural gas processing essentially depends on the gas composition [2, 3].

Gas flaring is the burning of unwanted produced natural gas, which cannot be processed or sold during oil and gas production and processing operations. In past decades, gas flaring was believed to be environmentally tolerable. However, scientists have found that the flaring of gas is an impediment to the environment; this has led to attempting to tackle the problem of gas flaring to advance it to an acceptable level worldwide.

Sprays and atomisation techniques have attracted the attention of many researchers and have been the subject of a wide range of theoretical and experimental studies during the past decade. Many studies concerning different aspects of sprays and atomisation have been performed and major advancements in spray analysis and spray characterisation have been made [4].

In this paper, the utilisation of natural gas that was previously flared was investigated experimentally using spraying and atomisation techniques for the generation of carbon nanotubes, by spraying simulated catalyst solution droplets into a hydrocarbon gas stream (*methane as a carbon source*) using a novel “atomiser device” incorporating pressure swirl atomisers. A furnace was installed underneath of “atomiser device” and the stream of droplet particles fell down through the furnace (400 - 800° C). Reaction inside the furnace occurred to produce the Single Wall Carbon Nanotubes (SWCNTs) materials and hydrogen as shown in Equation (1) and illustrated in Figure (1). The produced hydrogen could be used in fuel cell production for power generation.

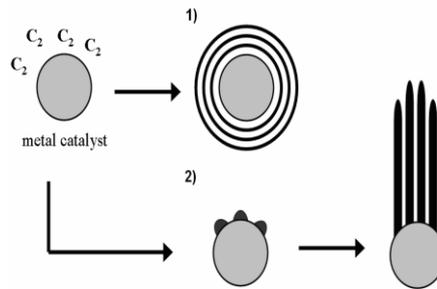


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These materials (SWCNTs) are mainly made up of 96.3% of carbon, 2.91% of carbon monoxide while other metal and non metal additives form the remaining 0.79%. The preliminary results of the experiments showed that it is possible to produce SWCNTs by using methane. This investigation involved a series of experiments which were undertaken to produce fine aerosol droplets that have a number mean diameter of less than or equal to 5  $\mu\text{m}$ . Water and air were used, in the first part, to simulate the metal catalyst and methane, respectively.

Traditional methods for producing SWCNTs involve growth from carbon vapour produced either by arc evaporation of metal-doped carbon electrodes, vapourisation of metal-doped carbon targets or by catalytic decomposition of molecules such as carbon monoxide and methane on supported metal particles. These methods produce SWCNTs in small quantities in a few hours hence there is the need to design equipment that should produce large quantities of SWCNTs.



**Figure 1** Proposed growth mechanism of carbon nanotubes on metal nanoparticles: 1) graphene sheets wrap around the nanoparticles 2) nucleation sites form on the nanoparticle surface which initiates the growth of carbon nanotubes

### Design procedures and Experimental Set-up

This section is discussed in two phases. The first phase describes the design of the atomiser used for the production of SWCNTs which was designed by the Spray Research Group (SRG) at the University of Salford, while the second phase describes the experimental procedure for the production of SWCNTs using the atomiser that was designed in the first phase. The second phase was realised in collaboration with the University of Oxford.

### Design Procedures

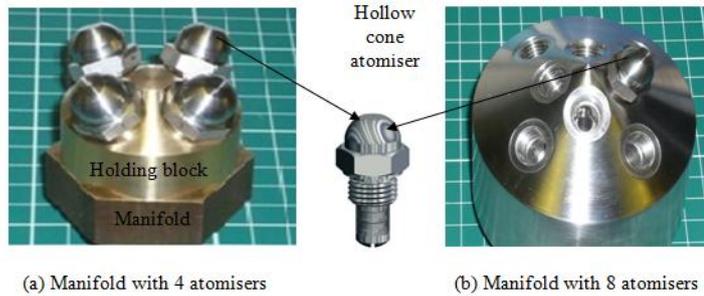
The commercial pressure swirl atomisers that are currently available are not able to produce drop size of  $\leq 5 \mu\text{m}$ . Therefore, it was necessary to design a system which could subsequently break-up the droplets to the required sizes. The first step in the design procedure is to compile the design specifications of the atomiser device, which are:

- Droplet size produced as small as possible ( $< 5 \mu\text{m}$ );
- Viscosity of aqueous phase about the same as water;
- Temperature up to 80  $^{\circ}\text{C}$ ;
- Rate of addition of aqueous phase 0.001-0.005 l/min;
- Rate of flow of methane 0.3 – 0.4 l/min;
- All methane or only a portion can be used for the atomiser and the rest can be added separately;
- Pressure of gas: the lower the better. Up to 1 bar, (0.1 MPa);
- Pressure of liquid up to 120 bar (12 MPa).

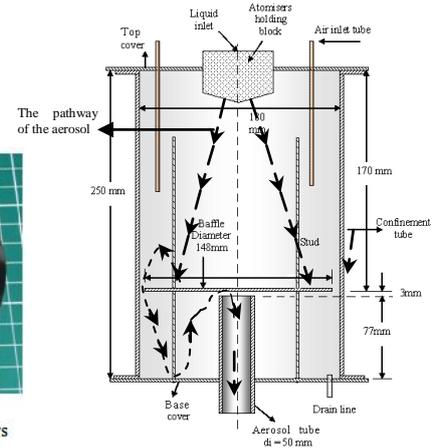
The design of the fine spray atomiser device for carbon nanotubes' production is partly based on the concept of "cascade impactors" method. Cascade impactors are widely used to classify particle sizes at different flow rates for industrial purposes [6, 7].

The atomiser device was designed to operate at low pressure and consisted of a confinement tube with a cover for each open end, into which they were screwed onto the tube; an atomiser holding block as shown in Figure 2, and a manifold of hollow cone commercial swirl atomiser that interacted with a baffle plate (or *impactor*) as shown in Figure 3. This baffle plate was used to separate the larger droplets and to produce a fine spray in the aerosol tube of the device. This is a novel method of producing fine spray droplets of  $\leq 5 \mu\text{m}$  using standard pressure atomisers. The confinement tube was constructed from perspex with dimensions: 250 mm length, 180 mm inside diameter and 3 mm wall thickness according to the design estimation as highlighted in [5].

On the centre of the top cover, an atomiser holding block of 50 mm diameter was fixed, for mounting the manifold of the four atomisers.



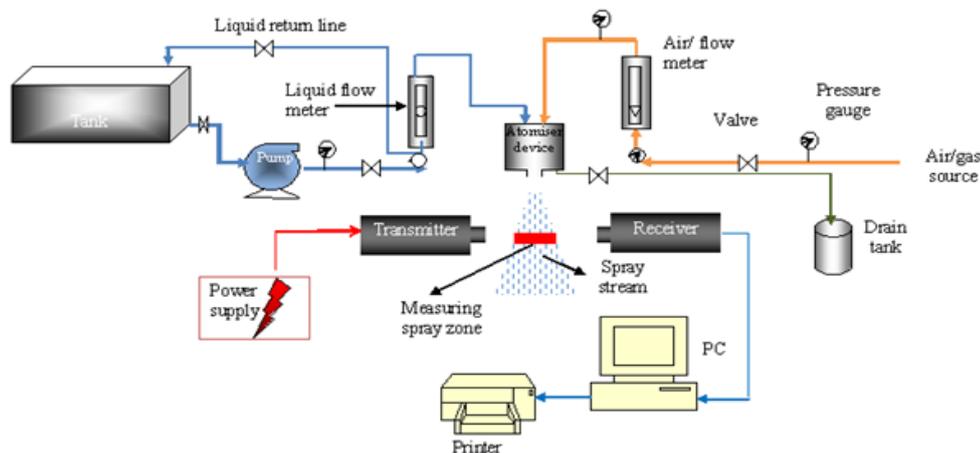
**Figure 2** Liquid spraying atomisers and holding block



**Figure 3** Optimum baffle plate (80 mm) and aerosol tube (77 mm) positions

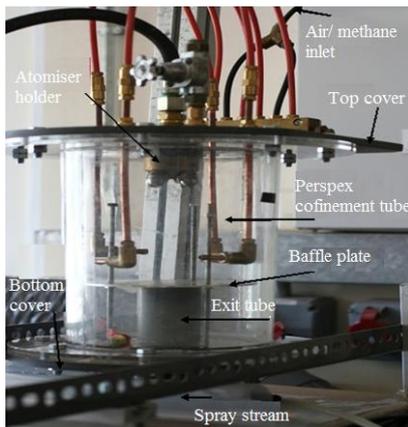
A hollow cone atomiser was selected because it has the finest drop sizes compared with full and flat cone atomisers. The atomiser has a nominal spray angle of  $60^\circ$  and exit orifice of 0.1 mm diameter. To incorporate the pressure swirl atomiser in conjunction with the cascade impactor conceptual idea imposed a design challenge. The atomiser holding and positioning assembly is made of iron and aluminium bars. It was designed and constructed to have free movement in relation to the Malvern Mastersizer-X (Malvern Instruments Ltd., Malvern, U.K) in order to enable testing of the atomiser at various positions as required, and also to avoid movement caused by tension in the flexible high pressure liquid supply pipeline.

### Experimental Set-up

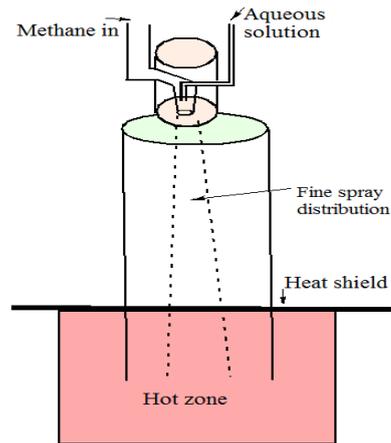


**Figure 4** Experimental set-up.

Figure 4 schematically shows the major components of the experimental set-up that were used in the corresponding trials. The system consisted of the following interrelated parts: reservoir tank, water pump, air supply and flow metering, atomiser holding and positioning assembly and atomiser device. A movable aluminium baffle plate, which could be moved up and down, with a 148 mm diameter and 2 mm thickness. This baffle plate was used to separate the larger droplets and to produce a fine spray in the aerosol tube of the device. This is a novel method of producing fine spray droplets of  $\leq 5\mu\text{m}$  using standard pressure atomisers. A movable tube (exit tube) of 50 mm diameter was also inserted in the centre of the bottom cover. The outlet side of this tube was reduced to 15 mm to narrow the spray stream slot. Both baffle plate and the tube were movable and their positions were changing during the trials in order to find the optimum set-up of the rig.



**Figure 5** Illustration of atomiser device set-up tested at the University of Salford.



**Figure 6** Schematic diagram of atomiser and furnace used at the University of Oxford.

Figure 5 shows the illustration of the atomiser device assembly, which was designed and tested throughout this investigation. The atomiser device was then mounted onto the furnace at the University of Oxford for production of SWCNTs as part of ongoing collaboration which is shown schematically in Figure 6. The apparatus consists of flowing methane over simulated metal catalyst in a reaction chamber at a temperature of about 800°C. Interactions between the methane and the catalyst result in the formation of carbon nanotubes as shown in Equation (1). The fabricated containment tube of the atomiser was reconstructed from non-shattering glass instead of Perspex with the same dimensions and a furnace (Carbolite type, STF 16/450 model) was installed at the atomiser's underside to allow the spray stream to fall down through the furnace (see Figure 6).

The atomiser device assembly (see Figure 5) was placed above the laser beam in a vertical position as the final optimum position. The atomiser device was mounted on the holding and positioning assembly and positioned at the required distance to spray through the laser beam of the Malvern Mastersizer-X. The laboratory lights were switched off during the spray measuring trials, since the detector is sensitive to external lighting and the lights could have influenced the measurement and thus the drop size distribution.

The pressure regulator on the methane supply line was adjusted to the operating working pressure of 1 bar (0.1 MPa) and its recommended flow rate was adjusted using the calibration charts [5]. The aqueous solution (liquid) pump was then started at the recommended pressure to deliver liquid to the spray head. The pressure was determined by the pressure gauge installed downstream of the pump outlet. The drop sizes were then measured and the results were subsequently recorded and post processed. Table 1 summarises the operating parameters that were used for all experiments during this study.

**Table 1** Operating parameters

<i>Parameter</i>	
Methane (Air) pressure, <i>MPa</i>	0.1
Methane (Air) flow rate, <i>l/min</i>	0.3 - 0.4
Liquid pressure, <i>MPa</i>	6 - 11
Liquid flow rate, <i>l/min</i>	0.001 – 0.005
Temperature, (room temperature) °C	20 – 25
Baffle plate position relative to base cover, <i>mm</i>	80 – 150
Baffle plate position relative to aerosol tube, <i>mm</i>	3 - 10
Atomiser device position relative to laser beam centreline, <i>mm</i>	40 – 100

All experiments were conducted at room temperature and by measuring the droplet sizes at different positions of both the baffle plate and the aerosol tube relative to the base cover and the atomiser device outlet relative to the laser beam centreline, in order to find the optimum arrangement of the rig apparatus. The Malvern Mastersizer-X results are presented in a series of figures and comparisons between some parameters, which are:

- The baffle plate and the aerosol tube positions inside the confinement tube;
- Water flow rate and pressure;
- Air flow rate and pressure;

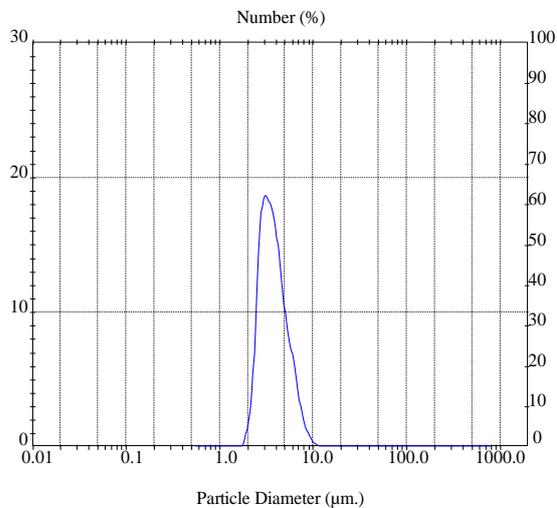
- Atomiser device position with respect to the laser beam.

## Results and Discussion

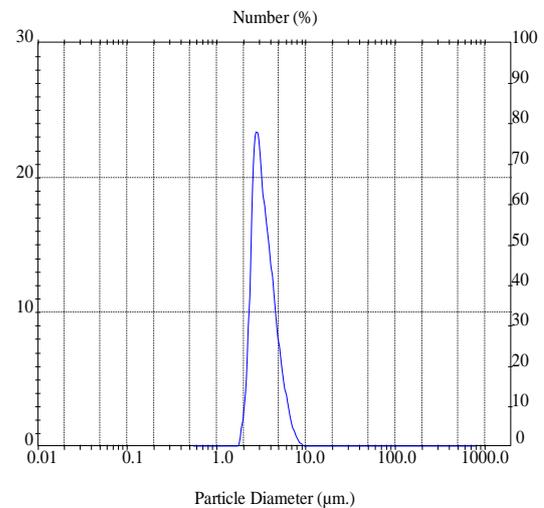
The atomiser device was designed to generate a fine aerosol stream with droplet sizes of less than or equal to 5  $\mu\text{m}$ , based on Number Mean Diameter (NMD) and compared with the Sauter Mean Diameter (SMD). Note that in the production of SWCNT, it is more important to consider the NMD of drops than the SMD, which is more related to mass surface and reaction processes. Moreover, using NMD ( $D_{n0.50}$ ) range of drop sizes includes smaller drops than SMD ( $D_{32}$ ).

### - Baffle Plate and Aerosol Tube Positions

This set of trials was carried out to find out the optimum position of both the baffle plate and the aerosol tube relative to the base cover of the atomiser device. When running the tests, the measurement was undertaken by placing the atomiser device perpendicular to the laser beam centreline initially at 100 mm. The baffle plate was tested at 150, 110 and 80 mm as measured from the base cover of the atomiser device, while the aerosol tube was kept below the baffle plate at 10 mm in the first two positions and 3 mm in the last one. In this set, the water supply pressure was set at 8 MPa and the flow rates of both water and air were maintained constant at 0.003 l/min and 0.3 l/min respectively. At the positions of 150 mm for the baffle plate and 140 mm for the aerosol tube, the atomiser device did not generate any aerosol stream. This was due to the long distance over which the aerosol stream had to flow. It must be emphasised that the tests were numbered as “SA-1, SA-2 ....etc.” in which SA referred to sprays and atomisation.



**Figure 7** Typical particle diameter ( $\mu\text{m}$ ) distributions for test AS-1.



**Figure 8** Typical particle diameter ( $\mu\text{m}$ ) distributions for test AS-6.

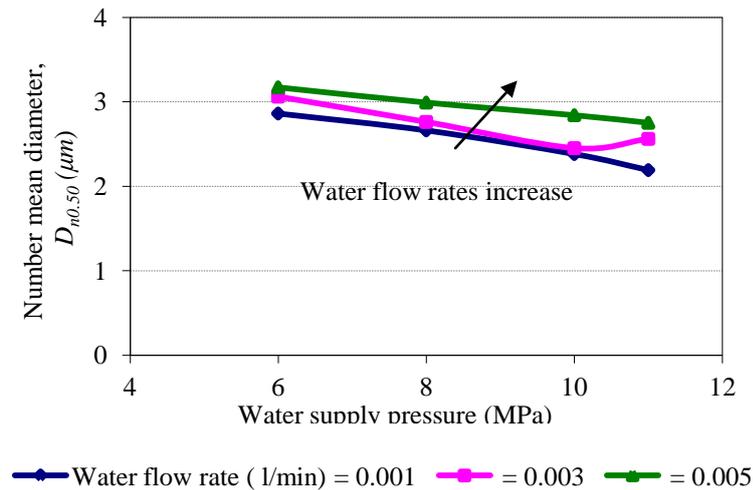
Based on these preliminary trials as there is no aerosol generated, it was decided to reduce the baffle plate and the aerosol tube positions to 110 and 100 mm respectively. In this trials' set, at the mentioned positions, the initial tests showed that fine sprays were generated and measured while crossing the laser beam (Figure 6, for test run AS-1). Figures 7 and 8 show typical particles diameter distributions for test AS-1 and AS-6.

The droplet size for AS-1 at baffle position of 110 mm was found to be 3.60  $\mu\text{m}$ , while at baffle position of 80 mm for AS-6 the drop size dropped to 3.22  $\mu\text{m}$ . From these results it is clear that the position of the baffle plate affects the droplet sizes, as they decrease with decreasing distance from the atomiser exit.

### - Water Flow Rate and Pressure

Series of experiments were performed at water (simulating the aqueous liquid catalyst for production of SWCNT) supply pressure varying from 6 to 11 MPa and its flow rate, varying from 0.001-0.005 l/min. The air (methane) pressure and flow rate were kept constant at 0.1 MPa and 0.3 l/min, respectively. Also the position of the atomiser device outlet was reduced to 75 mm from 100 mm with respect to the laser beam centreline, to improve the efficiency of collected aerosols.

Figure 9 shows the variation of the droplet sizes based on  $D_{n0.50}$  with water supply pressures for different water flow rates. As can be seen from this figure, it is clear that an increase in liquid (water) flow rate at constant supply pressure will increase the droplet size, while its decrease increases the droplet sizes.



**Figure 9** Variation of drop size ( $D_{n0.50}$ ) with water supply pressure for different water flow rates

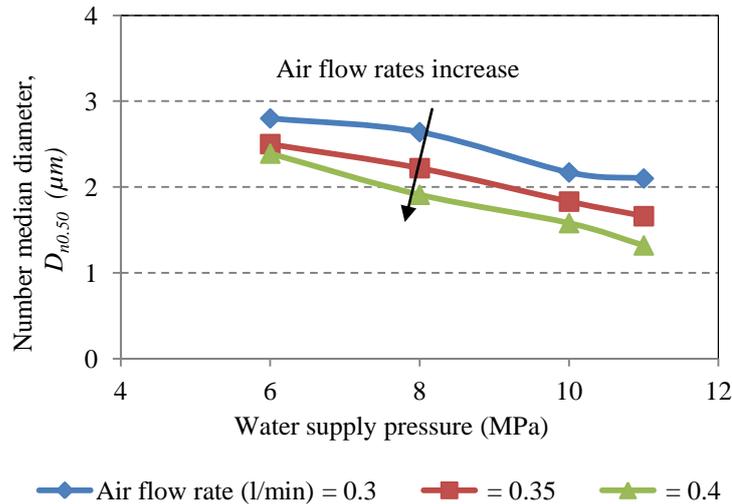
- **Air flow rate**

Air was used to simulate the methane. The effect of air flow rate on the droplet size distribution was investigated in this set, which varied from 0.3-0.4 l/min. The water supply pressure was varied from 6 to 11 MPa and its flow rate was maintained at 0.001 l/min. The position of the atomiser device outlet was kept the same as that of the previous set, at 75 mm with respect to the laser beam centreline. Table 2 presents the results of these experiments based on ( $D_{n0.50}$ ).

**Table 2** Typical results of air flow rates and water supply pressures on droplet sizes

Test No.	Water supply pressure, MPa	Air flow rate, l/min	$D_{32}$ , $\mu\text{m}$	$D_{n0.50}$ , $\mu\text{m}$
SA-19	6	0.3	5.79	2.80
SA-20		0.35	5.76	2.50
SA-21		0.4	5.56	2.39
SA-22	8	0.3	5.55	2.64
SA-23		0.35	5.13	2.22
SA-24		0.4	4.73	1.91
SA-25	10	0.3	5.98	2.17
SA-26		0.35	4.97	1.83
SA-27		0.4	5.72	1.58
SA-28	11	0.3	5.81	2.10
SA-29		0.35	5.53	1.66
SA-30		0.4	5.33	1.32

As can be seen from Figure 10, a decrease in the droplet size occurs as the air flow rate increases. This increase in air flow rate results in imparting a higher velocity to the water stream, which results in a break-up of the stream into finer fragments and thus reducing the droplet size.

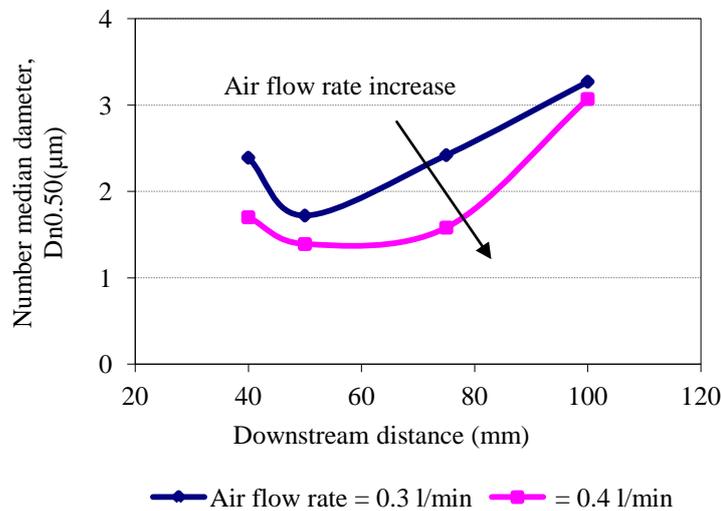


**Figure 10** Variation of drop size ( $D_{n0.50}$ ) with water supply pressure for different air flow rates

- **Atomiser Device Position with Respect to the Laser Beam**

This set of experiments was performed to investigate the effect of the atomiser position with respect to the measuring instrument. The runs were made with the atomiser device exit located at downstream distances of 40, 50, 75 and 100 mm with respect to the centreline of the analysing beam.

For each of these positions the pressure was kept constant at 10 MPa, the water flow rate was 0.001 l/min and the air flow rates were 0.30 and 0.40 l/min.



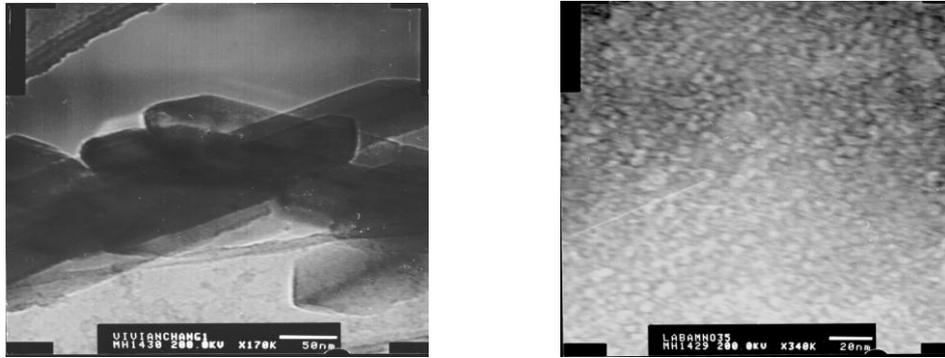
**Figure 11** Droplet size ( $D_{n0.50}$ ) as a function of downstream distance for 0.3 and 0.4 l/min air flow rates

Figure 11 shows the variation in droplet sizes as a function of downstream distance, for air flow rates of 0.30 and 0.40 l/min. It is clear that by decreasing the downstream distance at different water supply pressure, a decrease in droplet size occurs and vice versa. This may be due to coalescence and evaporation of smaller droplets. Also, it is clear that the increase in air flow rate decreases the droplet sizes, which confirms the previously obtained results. The upper curve gives the results of 0.3 l/min and the lower one gives those of 0.4 l/min, as the latter gave lesser droplet sizes.

From this, the result is true for distances of 50mm and over, but at 40mm a sudden drop size increase was noticed, which might be attributed to the very short distance to the measurement position. For shorter distances, the obscurescence level is so high for the laser beam travelling closer to the atomiser, that no light signal can be detected by the photodiodes.

- **Preliminary trials of SWCNTs production at the University of Oxford**

Using the experimental conditions above, the final investigation was performed at the University of Oxford using the designed atomiser from the University of Salford. Figure 12 shows the typical Transmission Electronic Microscopy (TEM) images obtained during this preliminary test run. SWCNT particles were deposited as products and were studied using Transmission Electronic Microscopy (TEM). These limited results provide further assurance that flare gas can be utilised to produce SWCNT using the novel design for the atomiser device. A number of further trials have been conducted and processed at the University of Oxford which will be published in due course.



**Figure 12** TEM images of the products of 2<sup>nd</sup> phase experiments

### Summary and Conclusions

The experimental study reported in this paper has examined the generation of fine aerosol sprays which have droplet sizes of less than or equal 5  $\mu\text{m}$ , produced from a designed atomiser device. This device assembly was designed for the purpose of SWCNT production. The produced aerosol stream had droplet sizes of less than 5  $\mu\text{m}$  as expected. The results have shown that the vertical position of the atomiser device with respect to the measuring droplet sizes' unit is the most suitable configuration compared with the inverted and horizontal positions as they did not generate any aerosol stream. The effect of water supply pressure and flow rate and the gas flow rate together with the downstream distance of the atomiser device on the droplet size distribution were investigated and characterised. In the second part, the preliminary results showed that it is possible to produce SWCNTs from natural gas (mainly  $\text{CH}_4$ ) that would have been flared by preliminary utilising the designed "atomiser device assembly". The utilisation of flared natural gas for SWCNTs production will reduce the  $\text{CO}_2$  emissions into the atmosphere.

### Acknowledgements

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