

## CHAPTER 7

### CONCLUSION AND FUTURE WORK

The key motivation in this research work is to develop carbon nanomaterials such as carbon nanotubes (CNTs) and graphitic nanofibers (GNF) and to test their feasibility as a medium to store hydrogen that works as an alternative fuel in onboard vehicle. The storage should be inexpensive, safe, low-weight tank, comparable in volume to a conventional gasoline tank with capability of quick loading and unloading hydrogen fuel. The hydrogen storage capacity target has been set by Department of Energy, USA to be 6.5wt%. However, due to uncontrollable parameters in synthesizing CNTs and GNFs such as the growth of larger diameter of the nanotubes and nanofibers due to agglomeration of catalyst particle at high reaction temperature, a higher surface area of developed material for better hydrogen capacity is hard to achieve. Nevertheless, this thesis work adds several significant contributions in this particular area of research.

#### 7.1 Contributions

By using Taguchi method as the design of experiment, the synthesis of iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ) and nickel oxide (NiO) catalysts are optimized using three controlled parameters that are calcination time, calcination temperature and the amount of the salt precursor, the most influential factor that affects the catalyst crystal size is the calcination temperature, that is the higher the temperature the larger the catalyst size. For the reaction yield of the catalyst, calcination temperature is the most significant factor that affects the  $\text{Fe}_2\text{O}_3$  reaction yield while the amount of salt precursor affects the NiO yield. Overall, the optimum conditions to produce the highest yield of the catalyst are at temperature of  $400^\circ\text{C}$ , calcination time of 4 hour and salt weight of 7g.

In synthesis of GNFs, for both preliminary and modified experiments all samples give the highest yield at the optimum reaction temperature of 600°C except for samples LFe at 700°C. the modified experiment has improved the GNF yield from 6.4 to 12.1 g/(g<sub>cat</sub>·hr) in iron-based GNF samples and from 32.9 to 60.2 g/(g<sub>cat</sub>·hr) in nickel-based GNF samples. Sample imaging observations using field emission electron microscopy (FESEM) and selected area diffraction of transmission electron microscopy (TEM) indicate that the synthesized GNFs have both platelet and herringbone structure with little CNTs at high temperature of reaction. Majority of the samples has a diameter range between 100–200 nm and the specific BET surface area varies from 60–290 m<sup>2</sup>/g. It is found that reaction temperature is the most influential parameter for the total surface area of the developed samples except for samples FG where the total surface area is highly affected by the C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub> flow. In general, the modified experiment has improved the reaction yield for both iron- and nickel-based GNFs but the nanofiber diameter range and the total surface area are remained unchanged in preliminary and modified experiments.

The development of CNTs has been extensively studied using floating catalytic chemical vapour deposition (FC-CVD) with benzene as the carbon source and commercial ferrocene as the catalyst. Three parameters that are reaction time, hydrogen flowrate and amount of catalyst have been closely controlled to produce multiwall nanotubes (MWNTs) with specific BET surface area between 50–120 m<sup>2</sup>/g and nanotubes diameter between 90 to 200 nm. At reaction temperature of 850°C, the optimum conditions to produce the highest yield of MWNTs are at reaction time of 40 minutes, H<sub>2</sub> flow rate of 300 ml/min and the catalyst weight of 0.3 g. The formation of CNTs is considerably cheap since the reaction takes place in less than 1 hour and the equipment set up is minimal. However, due to low surface area and tube encapsulation in most of the samples, the hydrogen adsorption process is unable to be applied.

The hydrogen adsorption measurement was carried using gravimetric measurement technique. At conditions of 77 K and 20 bar, the hydrogen adsorption capacities using the developed GNFs are found to be between 0.58 and 0.64 wt% as compared with a commercial SWNTs that give a hydrogen uptake of 1.07 wt%. Adsorption measurement at room temperature results in low hydrogen uptake. At 150 bar, the weight percentage of the adsorbed hydrogen using GNFs is ranging from 0.06 to 0.30 wt% while at 100 bar, the capacities ranging from 0.07 to 0.27 wt%.

The hydrogen uptake is proportional to the total surface area (i.e. specific BET surface area). However, certain isotherm results show that some samples with lower surface areas give higher hydrogen uptake. This is due to the higher micropore volume which provides more rooms for multilayer adsorbed hydrogen. Adsorption at cryogenic temperature (77 K) and moderate pressure (20 bar) provides higher uptake as compare to condition at room temperature (298 K) and at high pressure (100 bar). However, in reality the storage of hydrogen should be done at room temperature with pressure not more than 300 bar for safety aspects.

Based from the major thesis work, the specific contributions are highlighted as follows:

1. The optimization of CNTs and GNFs synthesis using Taguchi method as the design of experiment has successfully improved the yield of GNFs in particular with reaction temperature as the most influential parameter.
2. The optimization of  $\text{Fe}_2\text{O}_3$  and NiO catalysts has effectively produced a well accepted nanosized particle (within 20 to 60 nm) for the synthesis of GNFs and the catalyst crystal structure has resulted in platelet and herringbone structures of GNF.
3. An alternative way to determine the purity of CNTs and GNFs is from the Raman spectroscopy analysis where the degree of graphitization and relative value of amorphous carbon to graphite carbon can be determined.

4. The use of as-synthesized GNFs for hydrogen adsorption using gravimetric measurement technique in particularly intelligent gravimetric analyzer (at 77 K and 20 bar) and magnetic suspension balance (298 K, 150 bar) has competently produced hydrogen isotherm with stepped isotherm curve indicating layer-by-layer adsorption had been occurred on a uniform planar graphite surface.
5. Prediction of hydrogen isotherm curve at different surface areas using assumption-free model that is Neuro-fuzzy system had been achieved with error less than 8%.

## **7.2 Final conclusion**

The experimental results also show that it is hard to realize the target of 6.5 wt% set by Department of Energy, USA either at 77 K or 298 K. With or without modification of materials such as nitrogen-doped (Badzian, Badzian, Breval, & Piotrowski, 2001), purification (Viswanathan, Sankaran, & Aulice Scibioh, 2003), etc. the hydrogen uptake is still far from achieving the target. Nevertheless, it is crucial to develop materials with high micropore volume and narrow micropore size distribution for adsorption at 298 K. It is suggested that to achieve optimum hydrogen storage means that the capillary effect should be taken into consideration. It means that the pore size for hydrogen should be less than 1 nm. This is because with kinetic diameter of hydrogen molecules of 0.298 nm and it is expected that at least a monolayer of hydrogen adsorbed onto the surface.

## **7.3 Future work**

Feasibility studies should be done to improve the development of CNTs and GNFs for hydrogen storage application. The most important thing is to optimize controlled parameters so that the pore size distribution is narrow that is less than 1 nm and the micropore volume is large so that more hydrogen molecules could be occupied. A well controlled parameter could also result in more open pores rather than close

pores or tube encapsulation. This is because more open pores would result in higher surface area of the material.

Moreover, it is suggested that the flow rate of  $C_2H_4$  and  $H_2$  could be varied separately or it should be controlled one at a time to have a closer observation. In addition, new controlled parameters such as amount of catalyst used and different size of tube reactor to provide different residential time can be done to achieve optimum results. In addition, it is suggested that the analysis of the gas flow at the exit of the reactor to be analyzed continuously using mass spectrometer. This could optimize the reactant gas flow and hence can reduce gas wastage.

Despite of vast amount of researches have put on to study the purification of carbon nanomaterials, an extensive research should be carried out to investigate other development of carbon nanomaterials with limited pore size distribution between 0.6 to 1.0 nm. This can be achieved by studying how the crystallographic direction of carbon growth changes during the synthesis apart from optimizing the reaction parameters.

Besides hydrogen storage application, several GNF applications are possible for future research route. These includes fillers for conductive plastic resins, conductive nanocomposite in electrostatic painting, catalyst support in PEM fuel cell, nanocomposite reinforced adhesive and many more.