STATUS OF THESIS

Title of thesis	**SYNTHESIS, CHARACTERIZATION AND TESTING OF GRAPHITIC NANOFIBER FOR HYDROGEN ADSORPTION STUDY**

I _____SURIATI SUFIAN_____
(CAPITAL LETTERS)

hereby allow my thesis to be placed at the Information Resource Center (IRC) of Universiti Teknologi PETRONAS (UTP) with the following conditions:

1. The thesis becomes the property of UTP
2. The IRC of UTP may make copies of the thesis for academic purposes only.
3. This thesis is classified as

☐ Confidential

☑ Non-confidential

If this thesis is confidential, please state the reason:
_____
_____
_____

The contents of the thesis will remain confidential for _____ years.

Remarks on disclosure:
_____
_____
_____

Endorsed by

_____ _____
Signature of Author Signature of Supervisor

Permanent address:

8, Lorong Changkat Mewah 3
Taman Changkat Mewah
31000 Batu Gajah, Perak

Name of Supervisor
Assoc. Prof. Dr Suzana Yusup

Date : _____ Date : _____

UNIVERSITI TEKNOLOGI PETRONAS

Approval by Supervisor

The undersigned certify that she has read and recommend to the Postgraduate Studies Programme for acceptance, a thesis entitled "Synthesis, Characterization and Testing of Graphitic Nanofibers for Hydrogen Adsorption Study " submitted by Suriati Sufian in fulfillment of the requirements for the degree of Doctor of Philosophy (Ph.D.).

Date
21 January 2010

Signature: _____
Main Supervisor: Assoc. Prof. Dr Suzana Yusup

SYNTHESIS, CHARACTERIZATION AND TESTING OF

GRAPHITIC NANOFIBER FOR HYDROGEN ADSORPTION STUDY

by

SURIATI SUFIAN

Bachelor of Engineering (Hons) Chemical Process Engineering
with Fuel Technology
University of Sheffield, UK,1998.

Master of Engineering (Chemical Engineering)
University of Queensland, Australia, 2001.

A DISSERTATION

Submitted to the Postgraduate Studies Program
as a Requirement for the

Degree of Doctor of Philosophy (Ph.D.)
(Chemical Engineering)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR,
PERAK

JANUARY 2010

Declaration

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degrees at UTP or other institutions.

Signature: _____

Name: SURIATI SUFIAN .

Date: 21 January 2010 .

DEDICATION

This thesis is especially dedicated to my beloved family……

ACKNOWLEDGEMENTS

In the name of Allah, the Most Beneficent and the Most Merciful. I am indeed grateful to Him for guiding me on the right path and giving me the opportunity to study with strength, endurance and patience to complete this PhD study.

My sincere thank goes to my main supervisor, Assoc. Prof. Dr Suzana Yusup and co-supervisor Assoc. Prof. Dr Azmi Mohd Shariff for their guidance and support. Many thanks to Universiti Teknologi PETRONAS (UTP) for the scholarship and lab facilities, Ministry of Science Technology and Innovation (MOSTI) for the E-science research fund (Project No. 03-02-02-SF0020) as well as Assoc. Prof. Dr Fakhru'l Razi Ahmadun from Universiti Putra Malaysia (UPM) and Dr Gavin Walker from University of Nottingham, UK for giving me an opportunity to do collaboration work.

Not to forget, my gratitude to my research colleagues at UPM and University of Nottingham for helping me in initial lab work as well as the UTP Chemical and Mechanical Eng lab technologists for their kind assistance in samples' characterizations. My appreciation to Dr Shuhaimi Mahadzir (Chemical Engineering Program Head), Assoc. Prof. Dr M Ibrahim A Mutalib (ex-Director of REO), Chemical Engineering colleagues and my friends for their endless moral support. Also thanks to UTP support staff especially Human Resource Management, Finance Fund & Management, Research Enterprise Office and Postgraduate Studies for their co-operation throughout my PhD journey.

Most of all, to my husband Zuhairi Hj Baharudin, who is also finishing his doctoral study, thank you for your unconditional love, sharing pains with me and lightening burdens on me. To my lovely children, 5-year-old Nur Afiqah and 3-year-old Muhammad Syahmi, thank you for adding beautiful colors in my life. May Allah bless and protect them. Special thanks to my mother Hajah Hasnah Hassan, mother in-law Hajah Timah Soman and father Hj Sufian Kulob Ismail for their continuous prayers and encouragement. May Allah bless and reward them. Last but not least, to my late father in-law Allahyarham Hj Baharudin Sidik, may Allah bless his soul in peace and place his soul among the righteous in the Hereafter.

ABSTRACT

This research work focuses on the development of carbon nanomaterial particularly graphitic nanofibers by using chemical vapour deposition method. In addition, the development of catalyst for the synthesis of graphitic nanofibers has been investigated. For optimization of experimental parameters, Taguchi method has been used as the design of experiment. The capacity of the developed materials in hydrogen adsorption is tested at 77 K, 20 bar and 298 K, 100 bar using gravimetric measurement technique.

For graphitic nanofiber (GNF) development, the preliminary experiments show that the most optimum temperature to produce the highest yield for both iron- and nickel-based GNF samples is 600°C. Other controlled parameters are not significant except for C_2H_4/H_2 flow rate in nickel-based GNF samples synthesis where the maximum flow ratio (90/10) provides the highest yield in the reaction. In the GNF development, the modified experiment has improved the GNF yield from 6.4 to 12.1 $g/(g_{cat}.hr)$ in iron-based GNF samples and from 32.9 to 60.2 $g/(g_{cat}\cdot hr)$ in nickel-based GNF samples. In additions, the optimum conditions to synthesize the highest yield of carbon nanotube (CNT) is when CNTs are produced in the reaction time of 40 minutes, H_2 flow rate of 300 ml/min and the catalyst weight of 0.2 g using benzene as the carbon feedstock.

The sample characterization using scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM) has found that the average diameter size of CNTs varies from 90 to 210 nm and GNF varies from 100 to 200 nm. The use of transmission electron microscope (TEM) has proved that all CNTs are consist of multiwall nanotubes (MWNTs) while GNFs comprises of platelet and herringbone structures. Further characterization was done using Raman spectroscopy to obtain the purity of the sample by determining the relative value of amorphous carbon over graphite and the degree of graphitization. For the purpose of hydrogen adsorption study, the specific BET surface area of each sample is determined by surface area analyzer. The specific BET surface area of developed CNTs and GNFs are in the range of 51 to 121 m^2/g and 60 to 293 m^2/g, respectively.

For hydrogen adsorption studies at 77 K and 20 bar conditions, the capacities using the developed GNFs are found to be between 0.58–0.64 wt% while at 150 bar, the weight percentage of the adsorbed hydrogen using GNFs is ranging from 0.06–0.30 wt% and at 100 bar, the capacities ranging from 0.07–0.27 wt%. The method used for adsorption studies focused on gravimetric measurement technique because of its high accuracy and less amount of sample is required as an adsorbent as compared with the conventional method that is the volumetric measurement.

The experimental results also show that it is quite complex to realize the target of 6.5 wt% set by Department of Energy, USA either at 77 K or 298 K. Improvements in the development of CNTs and GNFs for hydrogen storage is a challenging task. Controlling the pore size distribution to be less than 1 nm and the micropore volume to be sufficient in enabling more hydrogen molecules to be stored are among the challenges. The presence of more open pores rather than close pores and tube encapsulation is very crucial.

ABSTRAK

Kerja penyelidikan ini memfokuskan pada penghasilan karbon nanobahan terutama nanofiber grafit (GNF) dengan menggunakan kaedah enapan wap kimia. Tambahan pula, penghasilan mangkin untuk sintesis GNF juga diselidiki. Untuk pengoptimuman parameter eksperimen, kaedah Taguchi telah digunakan sebagai reka bentuk eksperimen. Kapisiti penghasilan bahan untuk penjerapan hidrogen telah diuji pada 77 K, 20 bar dan 298 K, 100 bar dengan menggunakan teknik pengukuran melalui gravimetri.

Untuk penghasilan GNF, peringkat awal eksperimen menunjukkan suhu yang paling optimum untuk memperolehi pengeluaran yang tinggi untuk kedua-dua sample GNF yang dihasilkan berdasarkan besi dan nikel (sebagai mangkin) ialah 600°C. Kawalan parameter-parameter yang lain adalah tidak penting kecuali kadar aliran CH_4/H_2 dalam sintesis sample GNF berdasarkan nikel di mana kadar aliran maksimum (90/10) menghasilkan pengeluaran tertinggi dalam tindakbalas tersebut. Dalam penghasilan GNF, pengubahsuaian eksperimen telah meningkatkan pengeluaran GNF daripada 6.4 kepada 12.1 $g/(g_{mangkin}.j)$ untuk sampel GNF berdasarkan besi dan daripada 32.9 hingga 60.2 $g/(g_{mangkin}.j)$ untuk sampel GNF berdasarkan nikel. Tambahan, keadaan yang optimum untuk mensintesis pengeluaran nanotiub karbon (CNT) yang tinggi ialah apabila CNT dihasilkan dalam masa tindakbalas selama 40 minit, kadar aliran hydrogen sebanyak 300 ml/min dan jisim mangkin sejumlah 0.2 g dengan menggunakan benzin sebagai sumber karbon.

Pencirian sampel menggunakan mikroskop imbasan electron (SEM) dan mikroskop imbasan electron medan pencahayaan (FESEM) menunjukkan bahawa purata saiz diameter CNT ialah di antara 90 hingga 210 nm manakala untuk GNF ialah di antara 100-200 nm. Penggunaan mikroskop pancaran electron (TEM) menunjukkan bahawa semua CNT mengandungi nanotiub berbilang dinding (MWNT) manakala GNF terdiri daripada struktur tersusun (*platelet*/*stacked*) dan struktur tulang ikan (*herringbone*/*fishbone*). Pencirian selanjutnya dijalankan menggunakan spektroskopi Raman untuk memperolehi ketulenan sampel dengan mengira nilai relatif karbon amorfus kepada grafit dan tahap grafitisasi. Untuk

tujuan pengkajian penjerapan hidrogen, luas permukaan BET tertentu untuk setiap sampel dinilaikan oleh penganalisa luas permukaan. Luas permukaan BET tertentu untuk CNT dan GNF adalah masing-masing dalam lingkungan 51 hingga 121 m^2/g dan 60 hingga 293 m^2/g.

Untuk kajian penjerapan hydrogen pada keadaan 77 K dan 20 bar, kapasiti yang terhasil dengan menggunakan GNF yang dihasilkan didapati terhasil di antara 0.58–0.64 wt% manakala pada 150 bar, peratus berat hidrogen yang terjerap dalam GNF adalah di antara 0.06–0.30 wt% dan pada 100 bar, kapasiti tersebut adalah di antara 0.07–0.27 wt%. Kaedah kajian penjerapan memfokuskan kepada teknik pengukuran melalui gravimetri kerana kejituan pengukuran adalah tinggi dan sedikit sampel diperlukan berbanding dengan kaedah lama yang terdahulu iaitu pengukuran melalui isipadu.

Keputusan ujikaji menunjukkan bahawa adalah sukar untuk merealisasikan sasaran iaitu 6.5 wt% seperti yang telah ditetapkan oleh Jabatan Tenaga, Amerika Syarikat sama ada pada 77 K atau 298 K. Pengubahsuaian penghasilan CNT dan GNF untuk penyimpanan hidrogen adalah satu tugas yang mencabar. Pengawalan taburan saiz liang untuk kurang daripada 1 nm dan keberkesanan isipadu liang mikro untuk menyimpan molekul hidrogen adalah sebahagian daripada cabaran-cabaran tersebut. Kehadiran lebih banyak liang terbuka berbanding liang tertutup dan enkapsulasi tiub adalah sangat genting.

Incompliance the terms of the Copyright Act 1987 and the IP Policy of the university, the copyright of this thesis has been reassigned by the author to the legal entity of the university,

Institute of Technology PETRONAS Sdn Bhd.

Due acknowledgement shall always be made of the use of any material contained in, or derived from, this thesis.

© Suriati Sufian, 2010
Institute of Technology PETRONAS Sdn Bhd
All rights reserved

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Nomenclature

AC	Activated carbon
ANOVA	Analysis of variance
bc-MWNT	Bamboo concentric multiwall nanotube
BET	Brunauer-Emmett-Teller
bh-MWNT	Bamboo herringbone multiwall nanotube
CCD	Charged couple device
C-CNFs	Corrugated carbon nanofibers
CCVD	Catalytic chemical vapor deposition
c-MWNT	Concentric multiwall nanotube
CNF	Carbon nanofiber
CNO	Carbon nano-onion
CNT	Carbon nanotube
CVD	Chemical vapour deposition
CW	Continuous wave
DFT	Density functional theory
DoE	Department of Energy (of USA)
DOE	Design of experiment
DWNT	Double-wall nanotube
EM	Electron microscope
EOS	Equation of state
ESEM	Environmental scanning electron microscope
FC-CVD	Floating catalyst chemical vapor deposition
FDW	Fuzzy Design Wizard
FESEM	Field emission scanning electron microscope
FET	Field-effect-transistor
FFT	Fast Fourier Transform
FWHM	Full width at half maximum
GDP	Gross domestic product
GHP	Hydrophilic polypropylene membrane
GmbH	Gesellschaft mit beschränkter Haftung (a legal entity in Germany)
GNF	Graphitic nanofiber
HHV	Higher heating value
h-MWNT	Herringbone concentric multiwall nanotube
HRTEM	High-resolution transmittion electron microscopy
HT	High temperature
ICDD	International Centre for Diffraction Data
IGA	Intelligent gravimetric analyzer
IR	Infra-red
IUPAC	International Union Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
LCVD	Laser-assisted thermal chemical vapour deposition
LHV	Lower heating value
LNG	Liquefied natural gas
LO	Longitudinal optical
MARE	Mean absolute relative error

MSB	Magnetic suspension balance
MSD	Mean-squared deviation
MWNT	Multiwalled nanotube
n, m	Topological characterization of a nanotube by the chiral vector *nm*, where and span the graphite lattice
NCD	Nanocrystalline diamond
NGCC	Natural gas combined cycle
NGV	Natural gas vehicle
NIST	National Institute of Standards and Technology
OA	Orthogonal array
PEM	Proton exchange memberane
PETRONAS	Petroliam Nasional Berhad
PSD	Pore size distribution
QC	Quality characteristic
RBM	Radial breathing mode
RE	Renewable energy
SAED	Selected area electron diffraction
SEM	Scanning electron microscope
SET	Single electron tunneling
SI	Severity index
SNR	Signal-to-noise ratio
SPM	Scanning probe microscopy (includes STM, AFM, etc.)
SREP	Small Renewable Energy Power Programme
SWNT	Single walled nanotubes
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TISO	Two-Input-Single-Output
TO	Transverse optical
UHV	Ultra high vacuum
UV	Ultra violet
VOC	Volatile organic compound
VPSEM	Variable pressure scanning electron microscope
VSEM	Virtual scanning electron microscope
XRD	X-ray diffraction