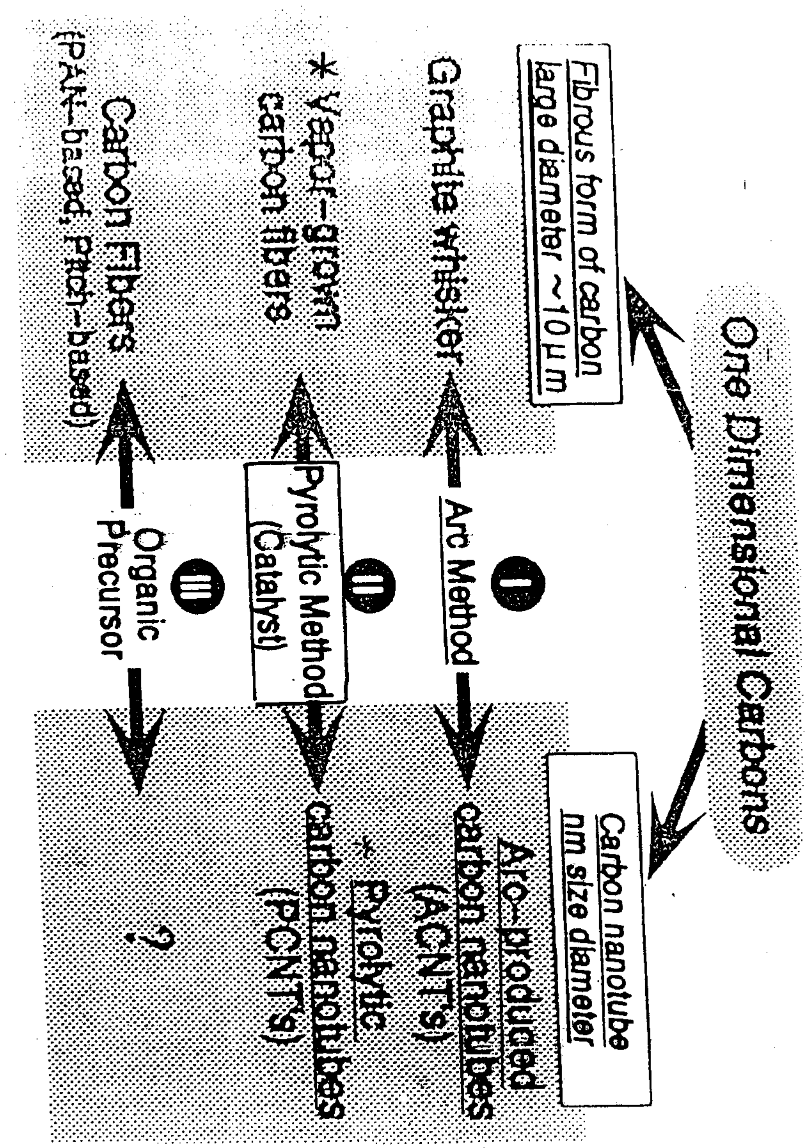


One Dimensional Carbon의 종류 및 용어

| Carbon Fiber | ~ 10 μm

Rayon, PAN(polyacrylonitrile), } spinning
Pitch(coal tar, petroleum)
VGCF(vapor grown carbon fiber) thickening

| Pyrolytic Carbon Nanofiber/Nanotube | 10 ~ 100 nm

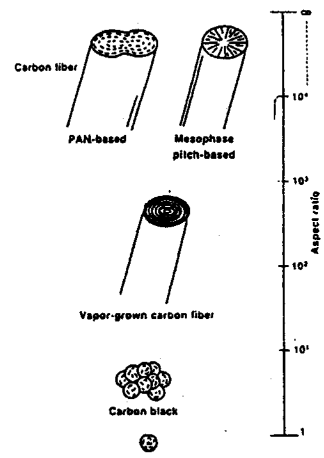
Carbon Filament(filamentous carbon)
VGCF(vapor grown carbon fiber)
Graphite Fibril/Nanofiber
low energy thermal, Catalyst

| Carbon Nanotube/Bucky Tube | 1 ~ 10 nm

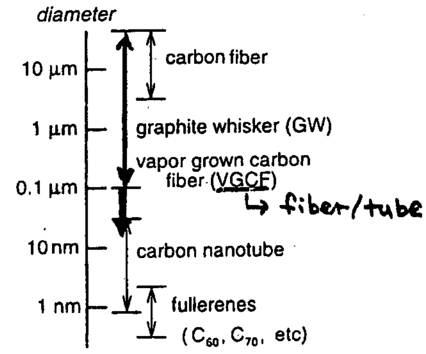
Arc method - Fullerene 제조법
high energy plasma

VGCF의 특징

Aspect ratio



Diameter



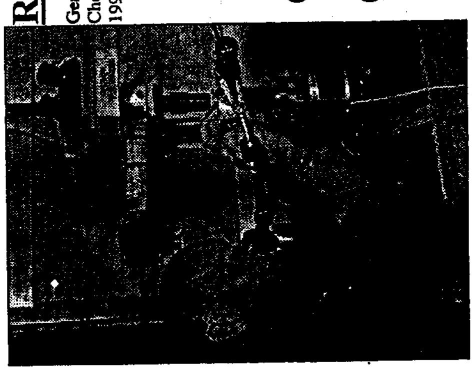
Richard E. Smalley Home Page

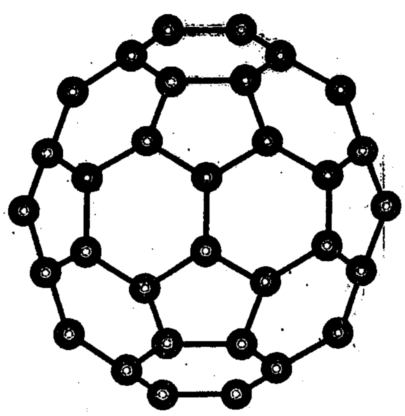
1ÀÉ/3ÀÉ

R.F. Curl
Kroto

Richard E. Smalley

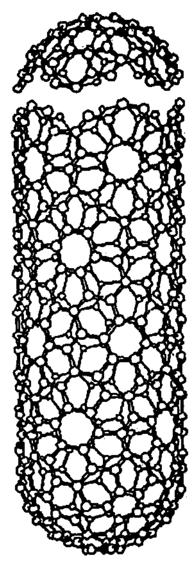
Gene and Norman Hackerman Professor of Chemistry and Professor of Physics
1996 Chemistry Nobel Prize Winner





Fullerene 1쪽/1쪽

Carbon Nanotube



Carbon Nanotube

Carbon Nanotube is a scroll of a graphene sheet. Nanotube can become both metallic and semiconducting depending on tubule diameter and chirality.

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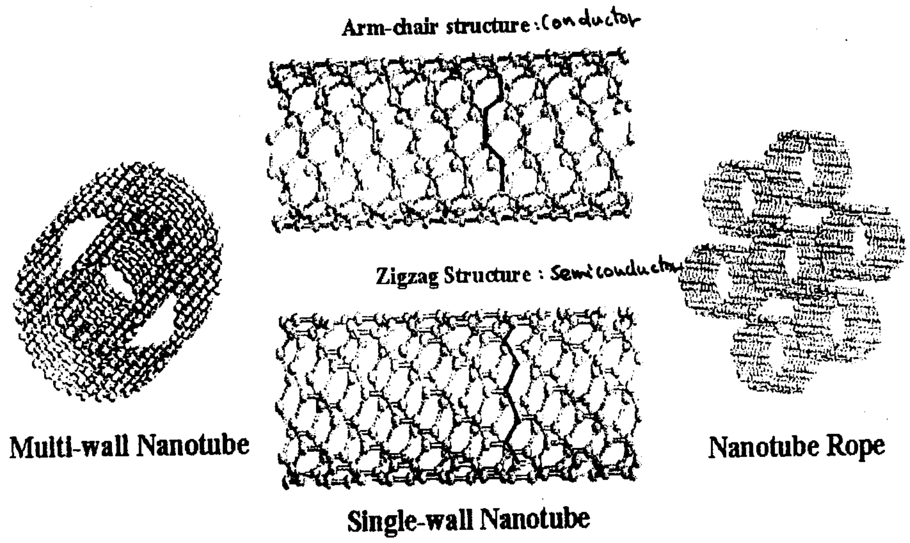


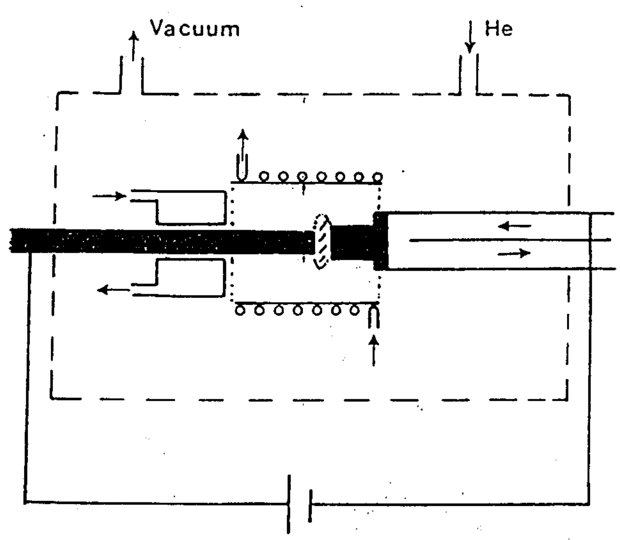


FIGURE 4.2 Schematic diagram of the arc apparatus where the nanotubes are formed from the plasma between the two black carbon rods. Except for the vacuum and He lines, all the arrows indicate the extensive water-cooling system of the apparatus. (Reproduced with permission from Ebbesen, T. W., *Annual Review of Materials Science*, 24, 235, 1994. Copyright 1994 by Annual Reviews Inc.)

Production of carbon nanotubes & nanofibers

① Multi-walled nanotube(MWNT): carbon arc method
direct current arc on the cathode
high temp. (~3700℃) Plasma

② Single-walled nanotube(SWNT): catalytic carbon arc method
carbon arc with composite anode
containig carbon and metal(Co, Ni, Fe)

③ Graphite nanofiber(nanotube): catalytic chemical vapor deposition
inexpensive production of high quality NT
low temp. technique
suitable for large scale production

Companies involved in both production and sales of nanostructured carbon materials

◆ Hyperion Catalysis International - Cambridge, MA, USA
◆ Catalytic Materials Ltd. - Mansfield, MA, USA
◇ Bucky USA - Bellaire, TX, USA
◇ Materials and Electrochemical Research Corp. - Tuscon, AZ, USA
◆ Applied Sciences, Inc. - Cedarville, OH, USA
◇ Dynamic Enterprises Ltd. - Twyford, Berkshire, UK

Characterization of carbon nanotubes & nanofibers

	Type	Method	Size	Price
MWNT	Tube	Carbon Arc	D: 2~15nm L: 1~10μm	$15/g
SWNT	Tube	Carbon Arc with Metal Catalyst	D: 0.7~1.2nm L: 2~20μm	$50/g
Graphite Fibril	Tube	Catalytic Chemical Vapor Deposition	D: ~10nm L: 1~10μm	-
Graphite Nanofiber	Fiber	Catalytic Chemical Vapor Deposition	D: 5~100nm L: 5~100μm	$4/Kg

※Purity of carbon nanotubes: 10~40%

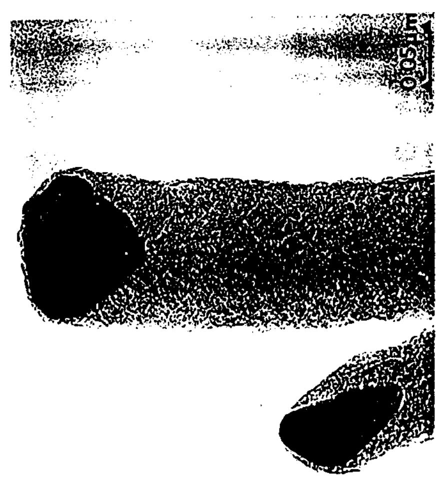
VGCF [vapor grown carbon fiber, carbon filament, carbon nanofiber(tube), carbon fibril etc.] 란?

탄소를 포함하는 가스(대부분의 탄화수소 및 일산화탄소)가 고온의 금속 표면에서 분해될 때 금속의 촉매 작용으로 형성되는 섬유형태의 탄소 물질

Hydrocarbons → $\underline{C}$ + $\underline{H_2}$

△, Cat. ☜ Ni, Co, Fe 및 그 합금들

Carbon monoxide → C + CO_2



VGCF의 종류 및 특성

a. High Temp. growth ~ 1200 C

- **fiber or tube** ○ **straight & long**
- **supported** ○ **expensive**
- **관련회사: Hyperion Catalysis Int'l, G.M.**

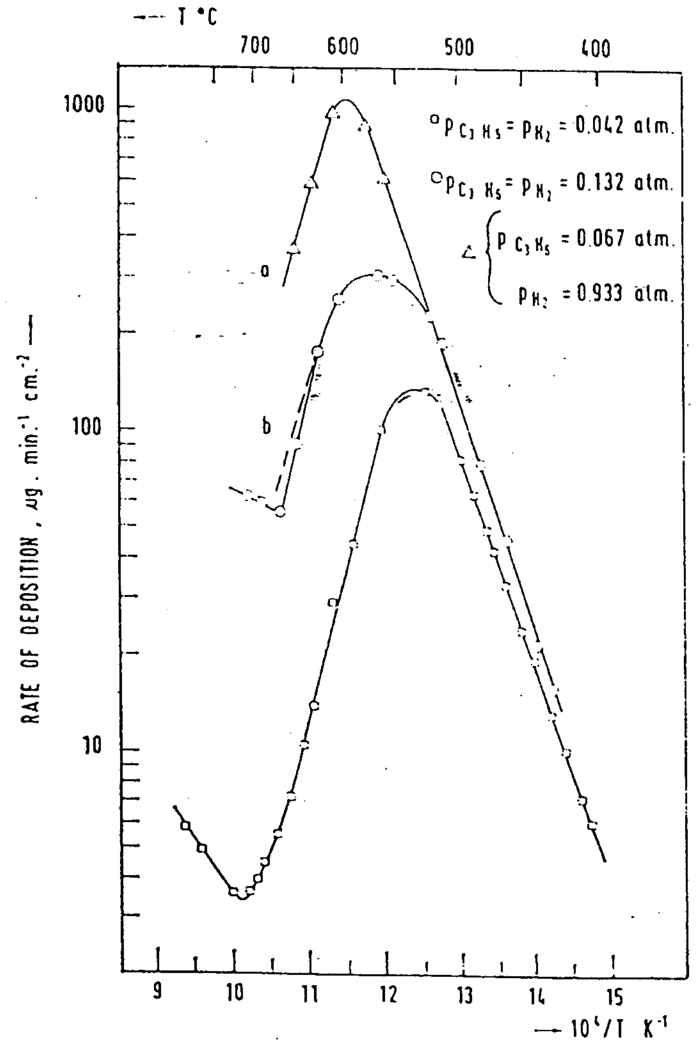
b. Low Temp. growth ~ 600 C

- **fiber** ○ **vermicular & short**
- **unsupported** ○ **cheap**
- **관련회사: Applied Science Inc. ,**
  Catalytic Materials, LTD.

In order to develop CCVD technique to grow true carbon nanotubes, careful study of many parameters affecting fiber morphology is needed.

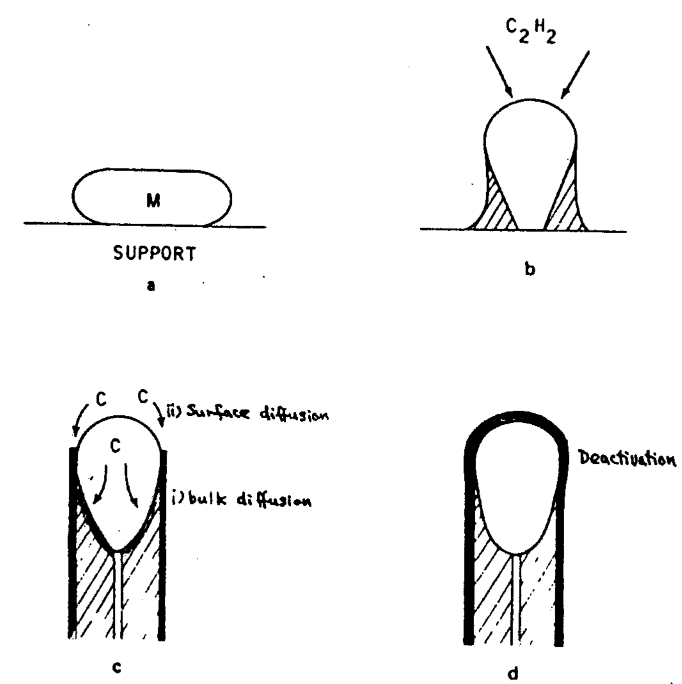
Catalytic Particles	Feedstock gas
Composition	Gas type
Initial size 1~10 nm	Gas mixture/composition
Initial shape	Flow rate
Particle support - Si, Al_2O_3	Pressure

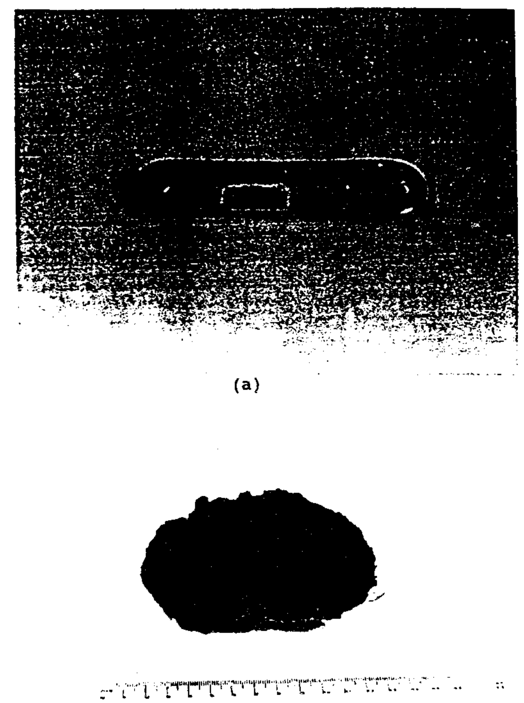
- Dr. R. S. Ruoff of Washington University
- Hyperion Catalysis International
- Dr. F. Derbyshire of University of Kentucky



3) Mechanism of Filament Growth

[Ref : J. Catal 26, 51 (1972)]

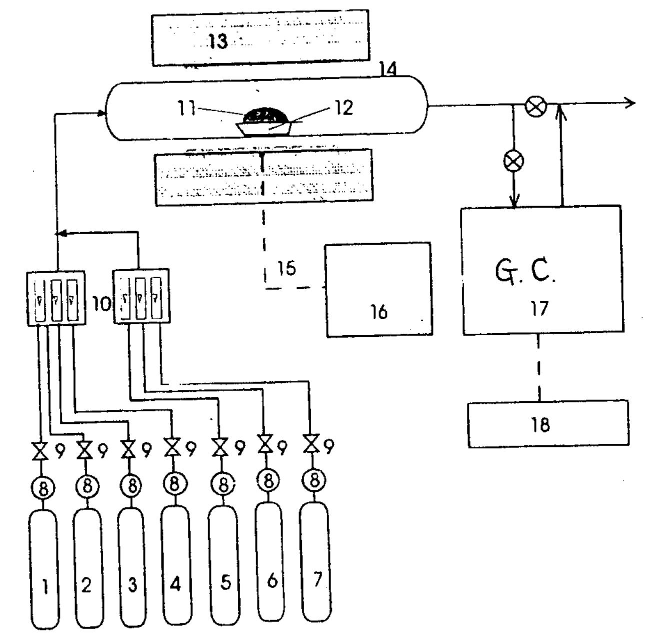




(a)

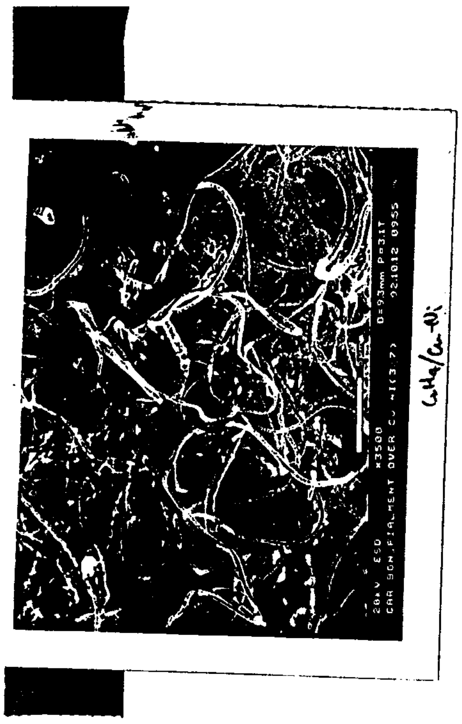
(b)

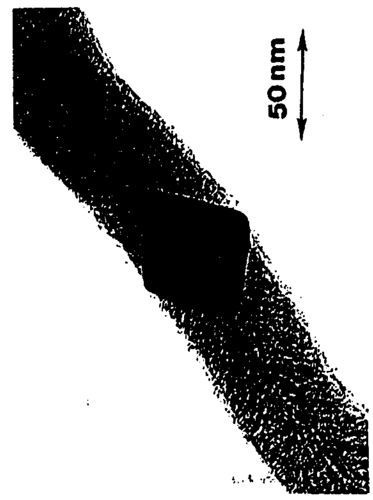
Figure 4-6. Typical Shape of Carbon Deposits: (a) Catalyst Amount before Reaction and (b) Carbon Deposits after Reaction.



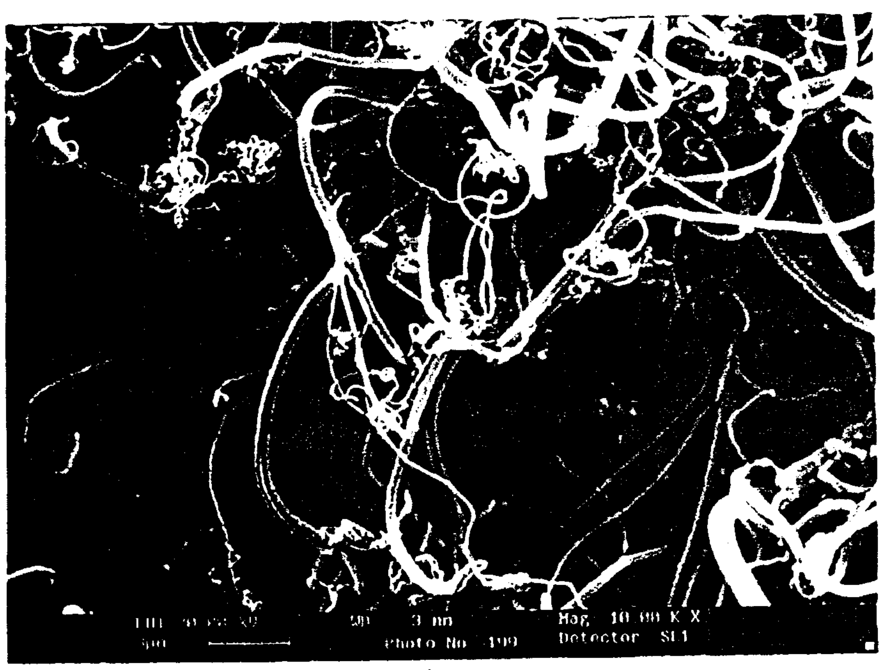
1. C2H4 Cylinder
2. C2H2 Cylinder
3. CH4 Cylinder
4. H2 Cylinder
5. CO Cylinder
6. H2S/He Cylinder
7. Helium Cylinder
8. 2-Stage Regulators
9. Needle Valves
10. Rotameters
11. Carbon Deposit
12. Ceramic Boat
13. Electric Furnace
14. Quartz Reactor
15. Thermocouple
16. Temperature Controller
17. Gas Chromatography
18. Recorder

Figure 3-1. Schematic Outline of Flow Reactor System.



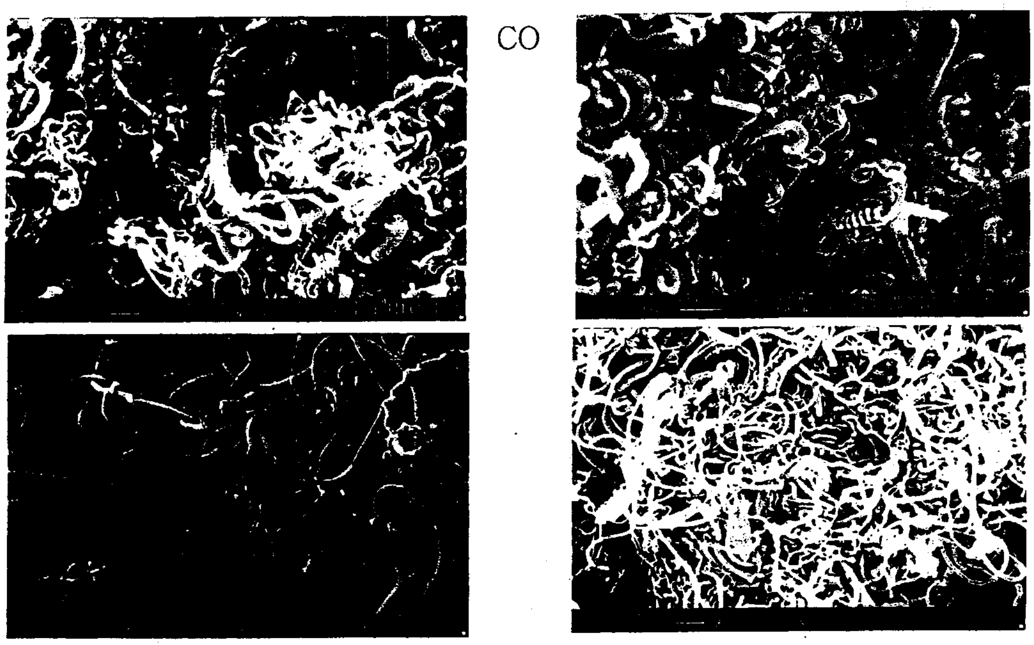


ure 4-8. A Typical Carbon Filament Showing a Diamond-Shaped Catalyst Particle within the Structure (produced from C_2H_2/Ni).

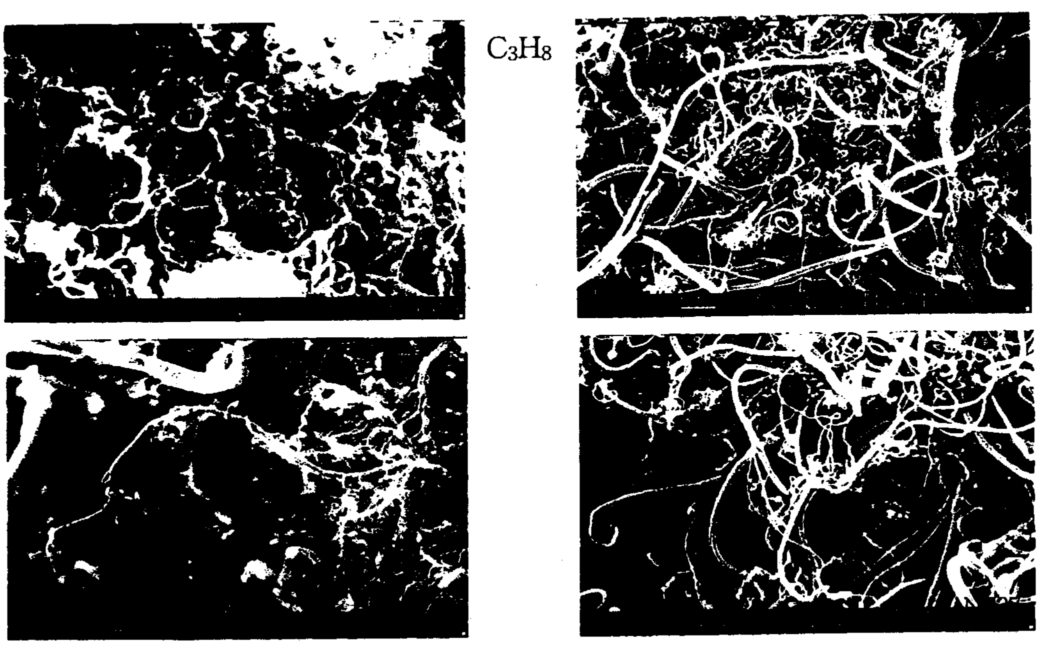


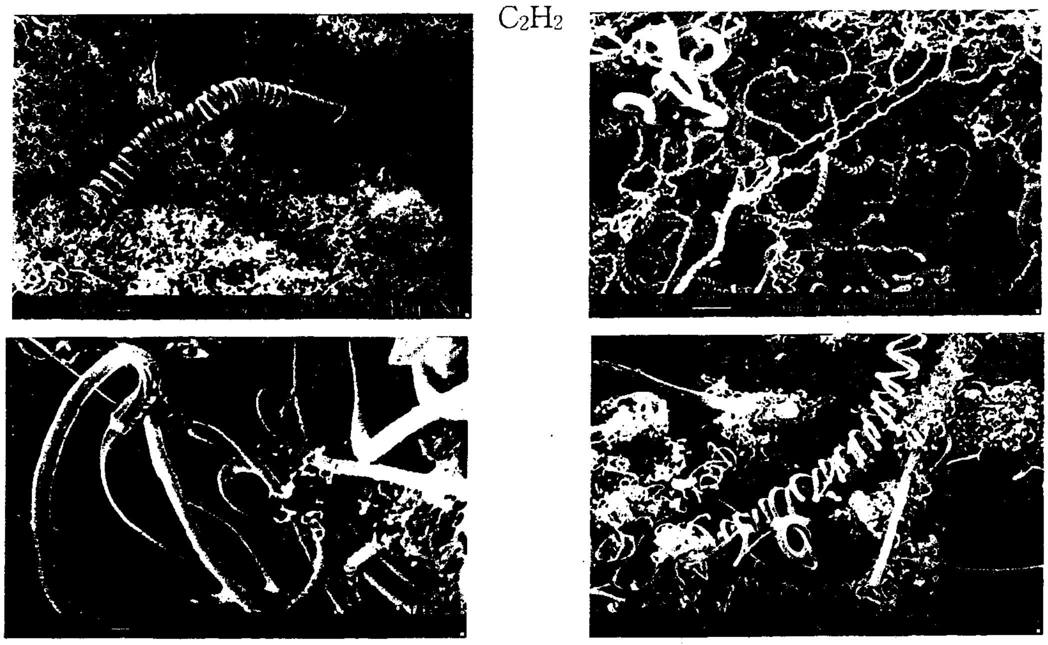
C_3H_8 / Ni-Cu (3:7)

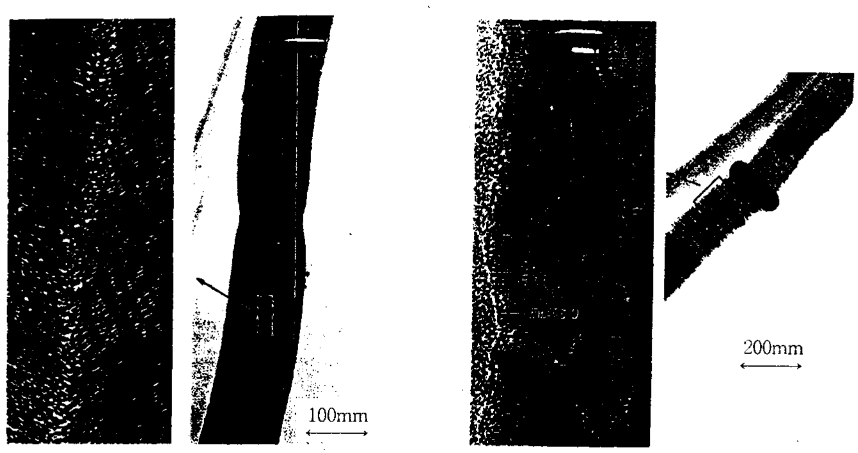
CO



C_3H_8







(a) Platelet type (b) Fish-bone type

TEM micrograph of carbon nanofiber produced from (a) CO-Fe(b) C_2H_4-FC73

Table 5-3. Yields of Various Products at 600 °C as a Function of Ethylene-Hydrogen Ratio

$C_2H_4:H_2$ Ratio	Product	Cu-Ni(3:7)	Ni
100:0	Methane	19.8	0.9
	Ethane	4.6	1.6
	Solid Carbon	74.3	-
	% Conversion	98.7	2.5
80:20	Methane	22.2	0.8
	Ethane	4.7	8.1
	Solid Carbon	72.0	58.0
	% Conversion	98.9	66.9
50:50	Methane	24.9	1.0
	Ethane	12.5	13.5
	Solid Carbon	57.9	44.2
	% Conversion	95.3	58.7
20:80	Methane	35.3	1.0
	Ethane	29.5	27.1
	Solid Carbon	26.8	31.6
	% Conversion	91.6	59.7

Table 5-4. Comparison of Product Distribution from Decomposition of Ethylene and Acetylene over Cu-Ni(3:7) and Ni at 600 °C, Carbon Atom Basis

Catalyst		Cu-Ni(3:7)		Ni	
Feed Gas (Torr)	Ethylene	100	-	100	
	Acetylene	-	100	-	100
	Hydrogen	-	-	100	100
	Helium	660	660	560	560
	Total	760	760	760	760
Product Yield (%)	Methane	14.65	1.60	0.39	1.32
	Acetylene	-	8.20	-	20.38
	Ethylene	5.63	0.33	53.33	2.13
	Ethane	3.92	0.04	5.48	0.40
	C3 Carbon	-	0.18	-	0.56
	C4 Carbon	-	0.05	-	0.91
	C5 Carbon	-	-	-	0.80
	Solid C	75.8	89.6	40.8	73.5
	Total	100.0	100.0	100.0	100.0
	% Conversion	94.37	91.20	46.67	79.62

Results

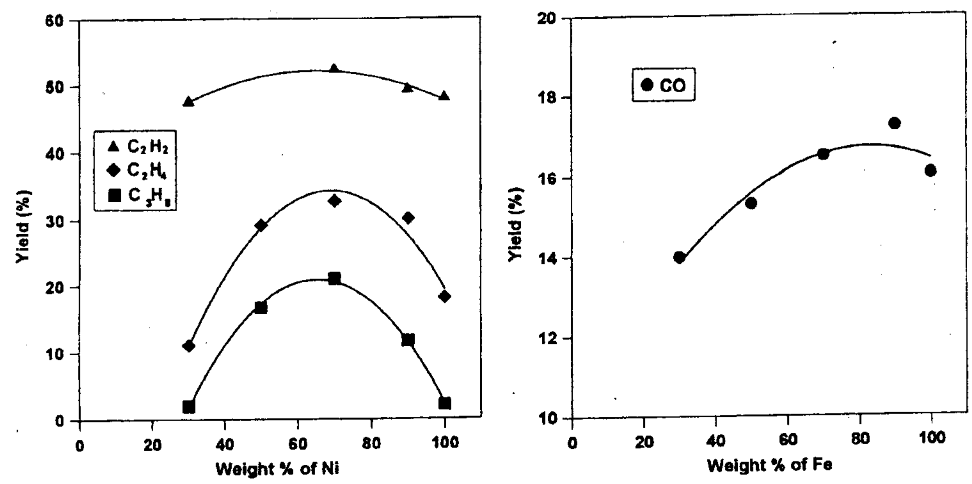


Fig. 1. Influence of catalyst composition on carbon yield with various carbon containing gases

Results

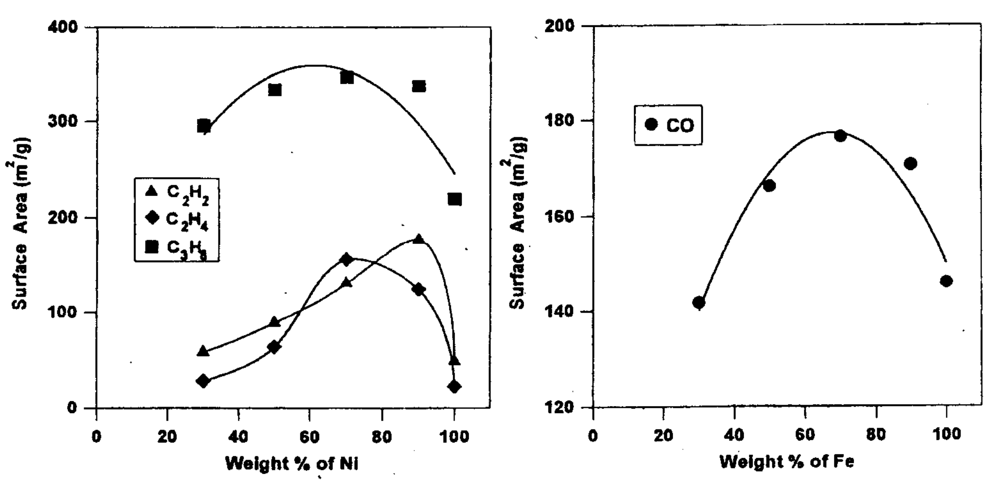


Fig. 2. Influence of catalyst composition on surface area of carbon deposits with various carbon containing gases

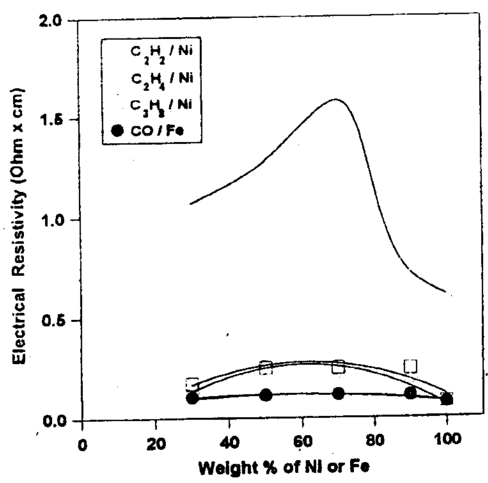


Fig. 4. Electrical resistivities of carbon nanofiber at 10000psi

			Electrical Resistivity (Ω x cm)	Apparent Density (g/cm^3)
Nano fibers from	Pure Ni	C_2H_2	0.609	1.36
		C_2H_4	0.041	1.49
		C_3H_8	0.079	1.38
	Pure Fe	CO	0.073	1.54
Graphite			0.015	1.9
A.C.	Rice Hulls (Steam)		5.57	1.44

Table 3. Comparison of electrical resistivities of carbon nanofiber with other materials at 10000psi

Myongji University *Carbon Materials Research Lab.*

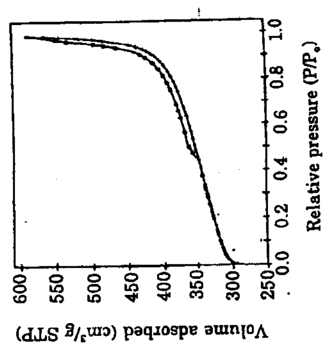


Fig. 2. Nitrogen adsorption (+) and desorption (o) isotherms for activated (970°C, 80 min.) carbon filaments.

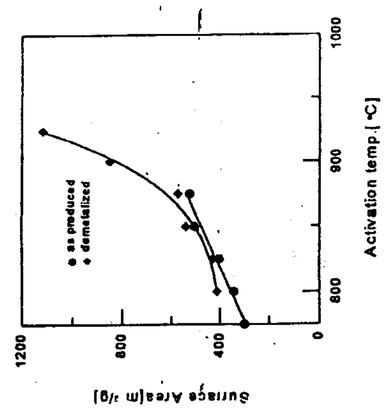
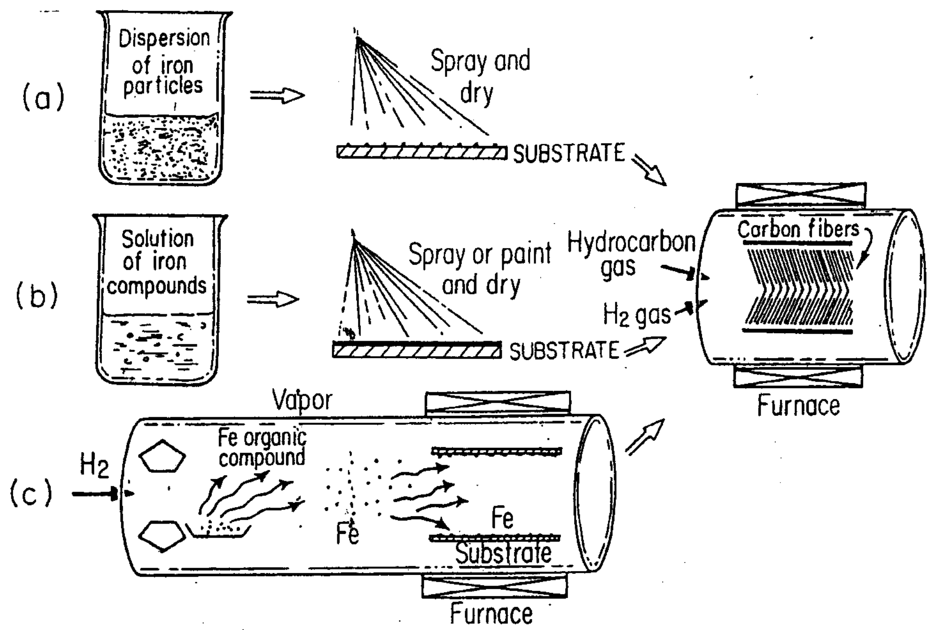
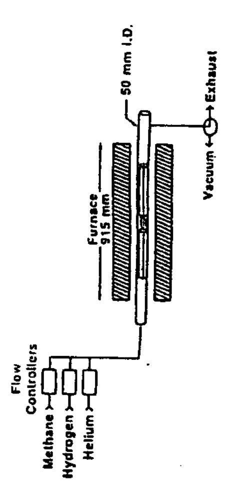


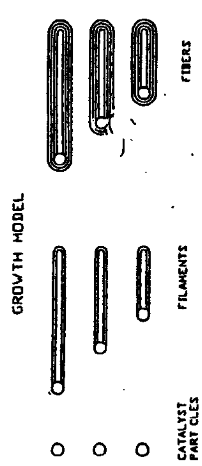
Table 2. Specific surface area, pore size and pore volume of carbon filaments before and after activation.

Activation condition	Specific surface area (BET, m^2/G)	Pore size (Å)	Pore volume (cm^3/g)			Yield (%)
			Total	Lower size range[a]	Upper size range[b]	
As-received	54.0 ± 0.3	81.7*	0.110	0.061	0.049	/
After O_3 exposure	40.7 ± 0.3	99.1+	0.095	0.041	0.055	100
970°C, 20 min.	218 ± 2	55.2+	0.257	0.091	0.166	76.4
1000°C, 20 min.	532.5 ± 8.5	52.6+	0.575	0.112	0.463	/
970°C, 40 min.	913 ± 16	55.0+	1.077	0.204	0.873	56.2
970°C, 60 min.	1121 ± 8	55.3+	1.323	0.249	1.074	48.2
970°C, 80 min.	1306 ± 16	55.3+	1.548	0.267	1.280	36.2
970°C, 100 min.	1214 ± 11	54.1+	1.493	0.257	1.236	30.1

* Mean pore size from 10 to 1000 Å.
+ Main pore size above 20 Å.
a Size below ~ 30 Å. See Fig. 1.
b Size above ~ 30 Å. See Fig. 1.







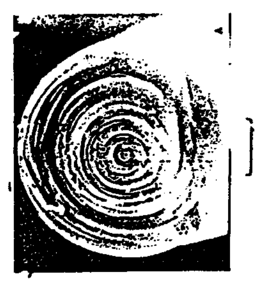


Figure 3. Fibers grown on inert semi-cylindrical substrates 30 c long and 4 cm inside diameter in the apparatus above.

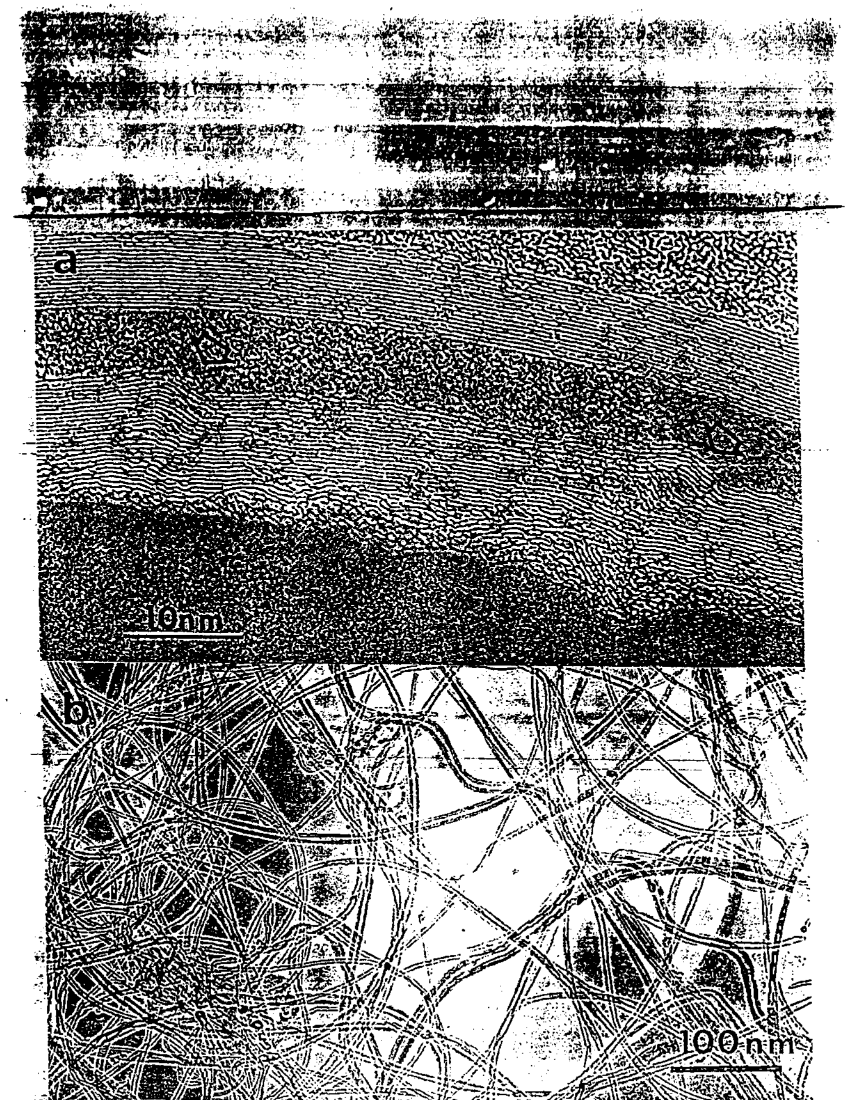
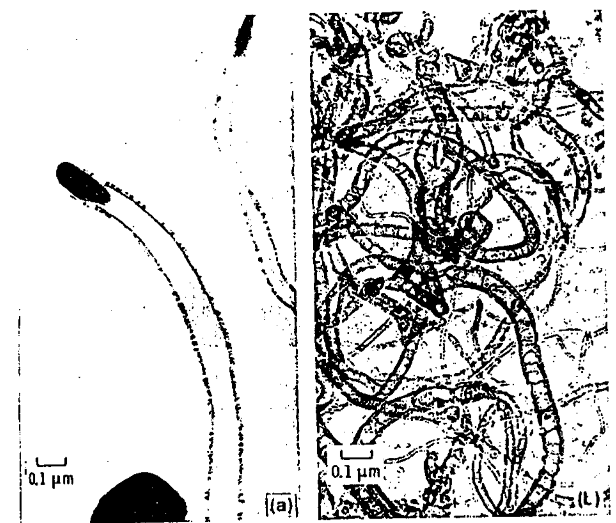
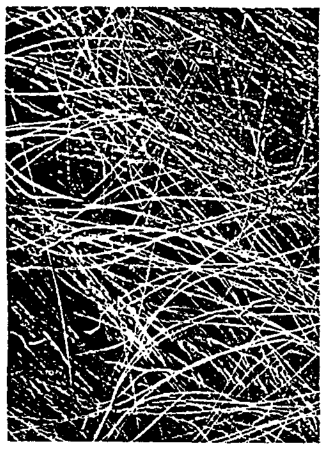


Fig. 9 Carbon nanotubules on Co–SiO_2: (a) HREM image showing defects in tubules; (b) helical tubules of various pitches between the straight tubules.



igure 2. a. Carbon fila ent grow from natural gas by an iron catalyst article at 970°C; b. a denser region on the same grid.



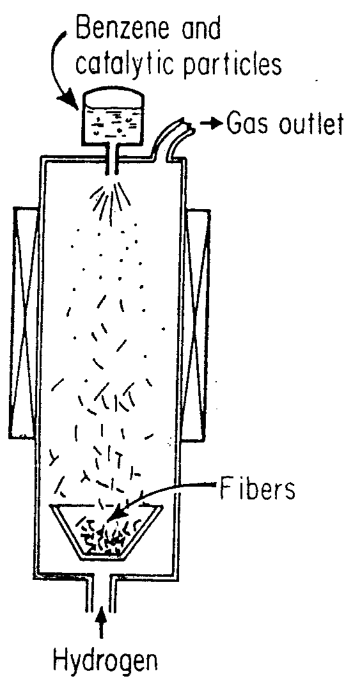
200 µm

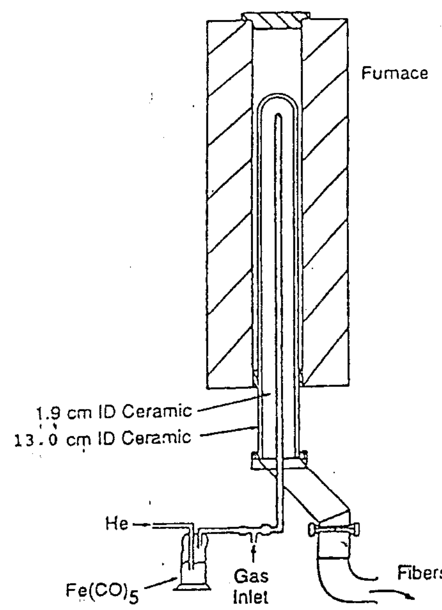
Table

Comparison of 7.5 µm diameter vapor-grown fibers with commercially available fibers.

Fiber	Density (g cm^{-3})	Tensile Modulus (GPa)	Tensile Strength (GPa)
Vapor grown	1.8	237	2.92
Carboflex*	1.6	55	0.69
P-55**	2.0	380	1.72
T-300**	1.76	228	3.45
T-600**	1.79	241	2.65

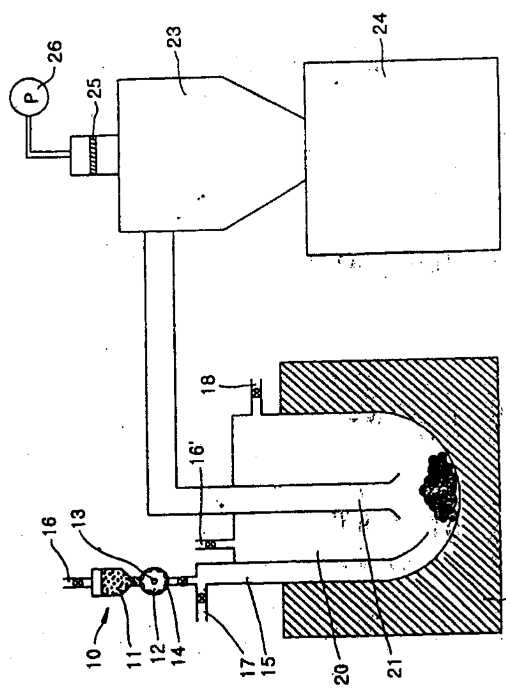
* Ashland Petroleum Company product information sheet.
** Union Carbide Corporation Technical Information Bulletin F-4934, Rev. 7, F-7001 and F-6374, Rev. 2.



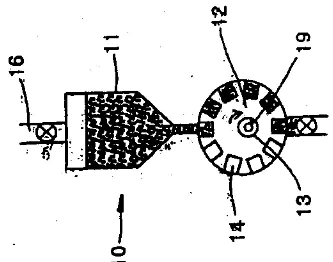


【도면】

【도 1】



【도 2】



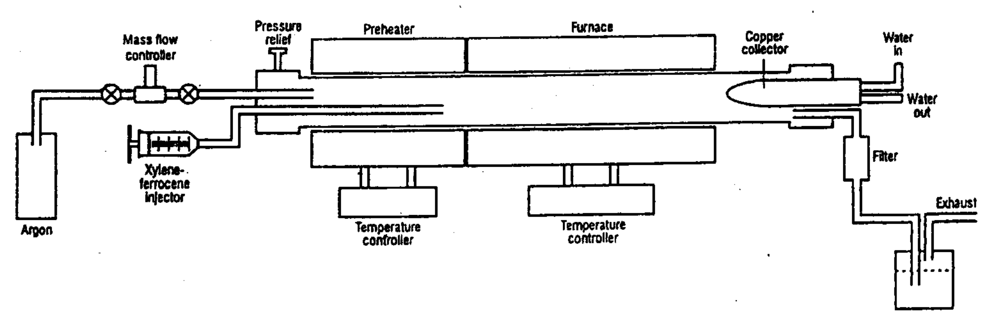
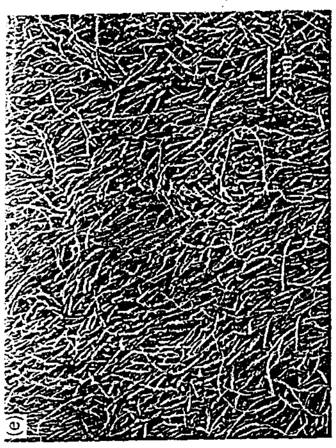
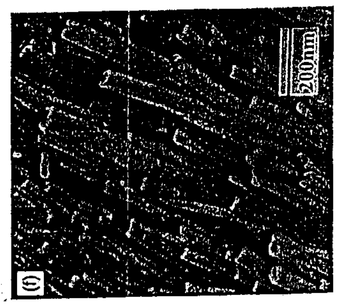


Fig. 1. Schematic of the reactor used for the nanotube synthesis. The ferrocene–xylene liquid feed is injected into the preheater stage using a syringe pump. Using a mass flow controller, Ar/H_2 gas is introduced at the entrance of the preheater to sweep the reactant vapors into the hot zone of the furnace.





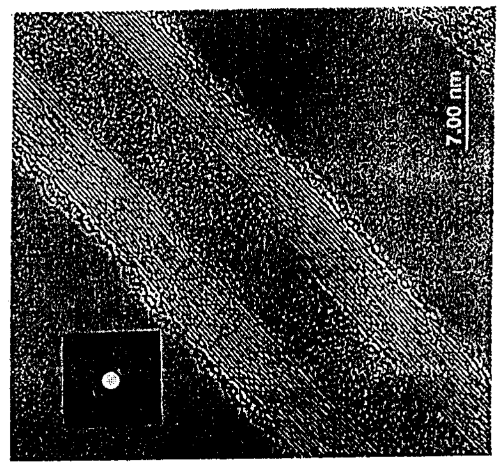


Fig. 3. HRTEM image (Phillips CM 200, 200 kV) showing the

Characterization of VGCF

- Examination by SEM & TEM
- Surface area & Pore size, volume analysis
- Degree of Graphitization
  - ~ X-ray diffraction - d-spacing
  - ~ Electronic property - electrical conductivity
  - ~ Chemical property - oxidation resistance
  - ~ Physical property - density