ORIGINAL PAPER

Abstract Carbon nanotubes, discovered in 1991, are a new form of pure carbon that is perfectly straight tubules with diameter in nanometers, length in microns. The conceptual designs of two processes are described for the industrial-scale production of carbon nanotubes that are based on available laboratory synthesis techniques and purification methods. Two laboratory-scale catalytic chemical vapor deposition reactors were selected for the conceptual design. One (CNT-PFR process) used the high-pressure carbon monoxide disproportionation reaction over iron catalytic particle clusters (HiPCO reactor), and the other (CNT-FBR process) used catalytic disproportionation of carbon monoxide over a silica supported cobalt–molybdenum catalyst (CoMoCAT reactor). Purification of the carbon nanotube product used a multi-step approach: oxidation, acid treatment, filtration and drying. Profitability analysis showed that both process designs were economically feasible. For the CNT-PFR process, the net present value, based on a minimum attractive rate

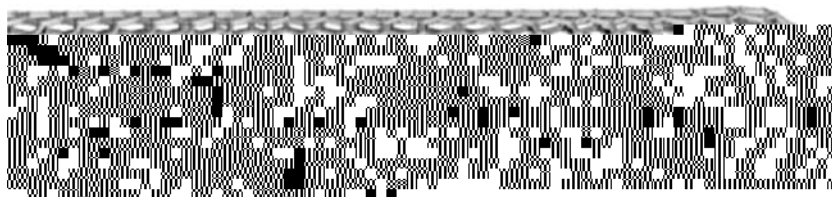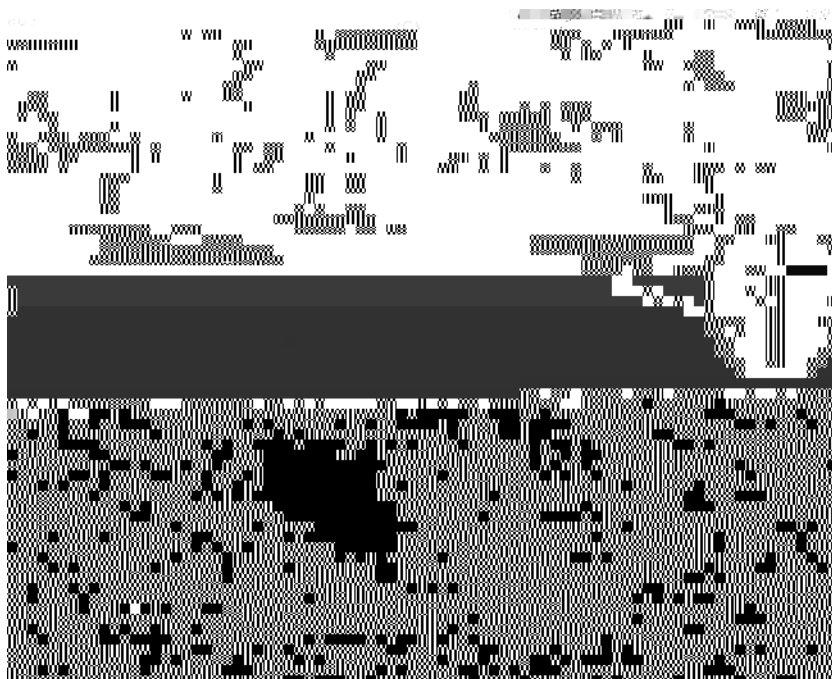Molecular model of a single-walled carbon nantube, from Terrones (2003)

Laboratory apparatus for production of carbon nanotubes

multi-wall carbon nanotubes (MWNT) to ten times this value for purified single-wall carbon nanotubes (SWNT). A laboratory apparatus and carbon nanotubes produced it are shown in Fig. 2. There are forty-four global producers of carbon nanotubes with a current global production of single-walled carbon nanotubes estimated to be about 9,000 kg/year. Presently, almost one-half of the multi-walled carbon nanotube production takes place in the United States, followed by Japan with ~40% of total production. Likewise, the United States leads production of single-wall carbon nanotubes with more than 70% total production capacity (Agboola 2005). The development of large-scale commercial production of carbon nanotubes at accessible costs is essential to emerging and potential carbon nanotube technologies.

In recent years, the interest in carbon nanotube has overshadowed that of fullerenes. Carbon nanotubes are not as readily available as fullerenes, and the number of researchers and groups working in the nanotube field has increased significantly. This has led to an exponential growth in the number of nanotube publications, going from 100 in 1994 to 1,500 in 2001 (Terrones 2003).

with tables describing key laboratory-scale reactors and purification methods to produce single and multi-wall carbon nanotubes.

Synthesis methods

The three main methods of producing carbon nanotubes are electric arc discharge, laser vaporization, and chemical vapor deposition and are described below. Other techniques include electrolytic synthesis, and a solar production method, among others and are reviewed by Agboola (

stant filtration volume. This was followed by washing with 6 M sulfuric acid to remove traces of any metal (mostly titanium) introduced into the sample from the ultrasonic horn. Purity greater than 90% was obtained with yields ranging between 30–70%.

Hernadi et al. (1996), reported the use of a combination of ultrasound and various chemical treatments in separating carbon nanotubes from the other impurities from carbon nanotube synthesis by catalytic decomposition of acetylene over supported Co/silica and Fe/silica. Dilute nitric acid (30%) was used to dissolve metallic particle (Co/Fe). Then sample was sonicated in a mixture of n-hexane, acetone and isopropanol. The purity and yield of carbon nanotubes generated from this purification technique were not reported.

Mechanical purification

Catalytic metal particles enclosed in carbon nanotube graphitic shells can be removed mechanically based on the ferromagnetic properties of the metal particles. The method of Thien-Nga et al. (2002) mixed SWNT suspension containing metal particles with inorganic nanoparticles in an ultrasonic bath that mechanically separated the ferromagnetic particles from their graphitic shells. The separated ferromagnetic particles were then trapped by permanent magnetic poles followed by a chemical treatment to obtain high purity single walled carbon nanotubes.
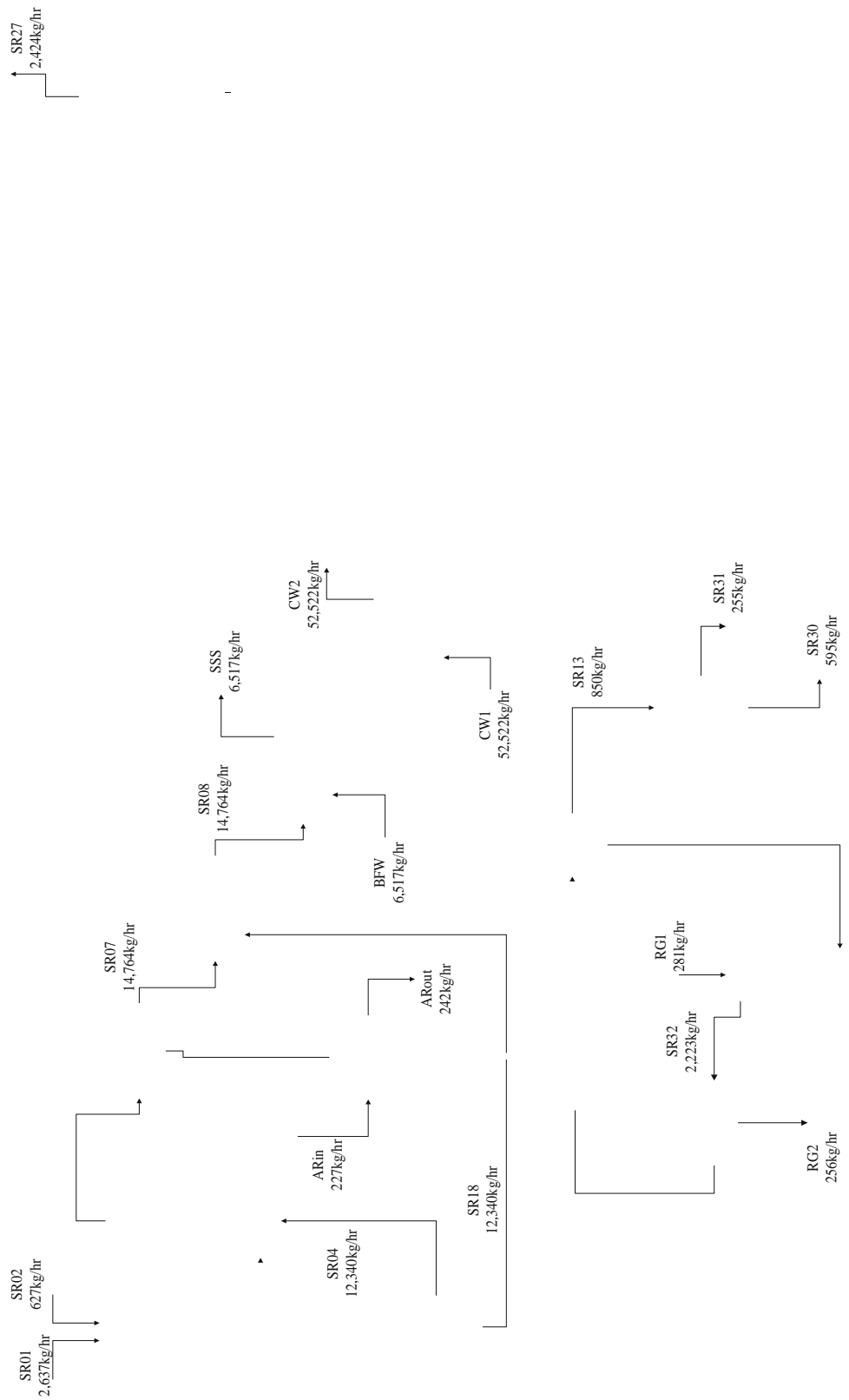
Functionalization

This purification technique is based on making single walled carbon nanotubes more soluble than the impurities by attaching functional groups to the nanotubes. The soluble carbon nanotubes can be separated from such insoluble catalytic impurities, and then the functional groups are removed. Georgakilas et al. (2002), described using 1,3-dipolar cycloaddition of azomethineylides in dimethylformamide (DMF) suspension to enhance the solubility of the functionalized single-wall carbon nanotubes while the catalytic metal particles remain insoluble. Amorphous carbon impurities also dissolve in the DMF suspension. The modified carbon nanotubes were separated from the amorphous carbon through a slow precipitation process that took place by adding diethyl ether to a chloroform solution of functionalized single walled carbon nanotubes. This process was repeated three times with the recovered soluble material, and the solid residue, containing the amorphous carbon impurities was discarded. The purified single-wall carbon nanotubes

were recovered by thermal treatment at 350 C, which eliminated the functional group attachments, followed by annealing to 900 C. The iron content in the impure single-wall carbon nanotubes and functionalized single-wall carbon nanotubes as measured by atomic absorption analysis was ~26% Fe (w/w) and ~0.4% Fe (w/w), respectively.

Microfiltration

This purification technique is based on size or particle separation that separates single-wall carbon nanotubes from coexisting carbon nanospheres (CNS), metal nanoparticles, polyaromatic carbons and fullerenes. A suspension of single-wall carbon nanotubes, CNS and metal nanoparticles is made using an aqueous solution with a cationic surfactant. The carbon nanotubes are subsequently trapped using a membrane filter, while other nanoparticles (metal nanoparticles and carbon nanospheres) passed through the filter. In this procedure (Bandow et al. 1997) a sample was soaked in organic solvents, such as CS_2, to dissolve and extract polyaromatic carbons and fullerenes. The CS_2 insoluble fractions were then trapped in a filter and then dispersed in an aqueous solution of 0.1% cationic surfactant (benzalkonium chloride) using ultrasonic agitation to separate the CNS and metal particles from the carbon nanotubes. After sonication for 2 h, the suspension was forced through a micro filtration cell using an overpressure (~2 atm) of N_2 gas, and a stirring unit was used to prevent surface contamination of the mem-

Process flow diagram
for the CNT-PFR design
(mass flow rates in kg/h)

SR27
2,424kg/hr

CW2
52,522kg/hr

SSS
6,517kg/hr

SR13
850kg/hr

SR31
255kg/hr

SR30
595kg/hr

SR08
14,764kg/hr

CW1
52,522kg/hr

BFW
6,517kg/hr

SR07
14,764kg/hr

RG1
281kg/hr

ARout
242kg/hr

SR32
2,223kg/hr

ARin
227kg/hr

RG2
256kg/hr

SR18
12,340kg/hr

SR04
12,340kg/hr

SR02
627kg/hr

SR01
2,637kg/hr

Process streams in the CNT-PFR process model (Refer to Fig. 3)

Name of stream	Description of process streams
SR01	Fresh CO feed to mixer (V-101)
SR02	Iron pentacarbonyl vapor to mixer (V-101)
SR03	Mixed CO and $Fe(CO)_5$ feed to reactor (V-102)
SR04	CO feed recycle from heater (E-100) to reactor (V-102)
SR05	Effluent stream from reactor (V-102) to filter 1 (Z-101)
SR06	Carbon nanotube from filter 1 (Z-101) to oxidizer (V-103)
SR07	Gas stream from filter 1 (Z-101) to heat exchanger (E-102)
SR08	Mixed gas stream from E-102 to waste heat b3h/lr t(E-102(oxidizer)-88.1((V-

des, is treated with 12% hydrochloric acid (HCl) solution (Meyyappan 2004). The iron oxide dissolves in the acid solution to form iron chloride ($FeCl_2$) and water. The ratio of the amount of iron oxide removed to the amount of HCl used is based on the reaction between iron oxide and HCl solution. However, since organometallics [$Fe(CO)_5$] are used to nucleate the carbon nanotubes produced, there will be some iron particles in the CNT-PFR carbon nanotube final product. The final carbon nanotube product will contain 97 mol% carbon nanotubes and 3 mol% iron (Bronikowski et al. 2001).

The nanotube slurry (SR12), containing the dissolved iron chloride, and carbon nanotubes is sent to the liquid–solid filter (Z-102), which separates the purified carbon nanotube product (SR13) from the iron chloride solution (SR14). The carbon nanotubes collected on the filter surface are washed several times with deionized water to remove any trace of hydrochloric acid from the carbon nanotube product. The washed, filtered and purified carbon nanotube product (SR13) is then dried at 800 K in the product drier (Z-103). The final carbon nanotube product (SR30), from the drier, is then sent to storage for packaging and sales.

The iron chloride solution (SR14) from the liquid–solid product filter is sent to an acid regeneration column (Z-104), where the hydrochloric acid solution is regenerated. The iron chloride solution is oxidized in the column to produce hydrochloric acid and iron oxide residue. The iron oxide residue produced is saturated with hydrochloric acid and is removed from the acid solution in the centrifuge separator (Z-106) which is sent to off-site treatment (http://www.acidrecovery.com). The recovered hydrochloric acid (SR15) from the centrifuge is recirculated back to the acid treatment tank (V-104) for another reaction cycle.

Absorber section

The process units in the absorber section include: a gas absorber (T-101), a gas stripping column (T-102), and a cross heat exchanger (E-105). Other process units include a kettle reboiler (E-106), a flash drum (V-105) and a discharge/vent valve (Z-105). The carbon dioxide produced during the CO disproportionation reaction over catalytic iron nanoparticles is absorbed in the counter-current flow of monoethanol amine (MEA) solution in the gas (CO_2) absorption column.
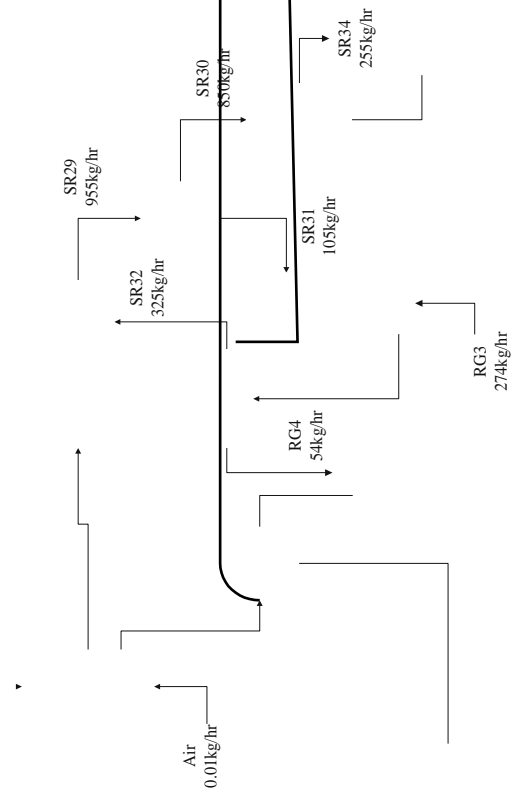
The mixed gas stream (SR10) from the heat exchanger water cooler (E-104), containing CO_2 and unconverted CO, enters the gas absorption column as

This design is based on carbon monoxide dispropor-
tionation over mixed cobalt–molybdenum catalyst on
silica support in a fluidized bed reactor developed at
the University of Oklahoma. The reaction forms car-
bon nanotubes and carbon dioxide at temperatures
between 973 and 1,223 K, and total pressure ranging
from 15 to 150 psia. The conversion of CO is 20 mol%,
and the carbon monoxide selectivity is 80% (Resasco
et al. 2001). The process flow diagram for the CNT-
FBR process is shown in Fig. 4, and the mass flow rates
on the PFD are in kg per h. The descriptions of the
process units and streams in the process flow diagram
are given in Tables 3 and 4. The process consists of the
feed preparation section, the reactor section, the ab-
sorber section and the separation/purification section.

Feed preparation section

The process units in the feed preparation section in-
clude the heater (E-201) and the gas compressor (C-
201). Fresh CO feed stream (SR01) at 303 K is
combined with the CO feed recycle stream (SR17) at
490 K in the gas-fired heater (E-201). The make-up
CO feed stream (SR01) consists of 3,471 kg/h of CO
at 490 K, while the gas compressor (C-201) supplies
13,883 kg/h of CO feed recycle (SR17) to the heater
at 490 K and 150 psia. The combined CO feed stream
(SR02) is fed into the fluidized bed reactor (V-201) at
1,223 K and 150 psia. The temperature of the combined
CO feed stream (SR02) leaving the heater is at 1,223 K,
and the stream is sent to the reactor (V-201). The
operating conditions in the reactor are maintained t hsm2he
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Process flow diagram
for the CNT-FBR design
(mass flow rates in kg/h)

SR29
955kg/hr

SR30
850kg/hr

SR34
255kg/hr

SR31
105kg/hr

SR32
325kg/hr

RG3
274kg/hr

RG4
54kg/hr

Air
0.01kg/hr

Process units for the CNT-FBR process (Refer units

Process Streams in the CNT-FBR Process (Refer to Fig. 4)

Stream	Process stream description
SR01	
SR02	
SR03	
SR04	
SR05	
SR06	
SR07	
SR08	
SR09	
SR10	
SR11	
SR12	
SR13	
SR14	
SR15	
SR16	
SR17	
SR18	
SR19	
SR20	
SR22	
SR23	
SR24	
SR25	
SR26	
SR27	
SR28	
SR29	
SR30	
SR31	
SR32	
SR33	
SR34	
Utility streams	
AK1	
RGS1	
RG4	
BFW and SST	
CW5 and CW6	
WS1	
RG4	

(SR19) enters the top of gas stripping column (T-202) at 393 K. Carbon dioxide gas is steam stripped from the solute-rich solution in the gas stripper. Saturated steam is supplied to the reboiler (E-205) for gas stripping from the waste heat boiler (E-202).

The carbon dioxide (SR25) thus stripped, leaves the stripping column at the top and is sent to the flash drum (V-204) where any liquid entrainment in the vapor stream is recovered and returned to the gas stripping column. The CO_2 gas stream (SR27) which is

Summary of the process units used in the conceptual

economic price is estimated from the total product cost $_T$, the annual cost of capital, EUAC annual capital expenditures $_{cap}$, and production rate.

The net present value is used to compare similar projects tha-225.l5s(a20m7.142 690.916 238.1-93.1(process)]TJEMC /TD <</MCID 8 >>Bar)-8.x 3u 238.1value i9c>>BDC /T1

Summary of the profitability analysis for the conceptual designs of CNT processes

Economic analysis Index	HiPCO process	CoMoCAT process