Conceptual Design of Continuous Processes for Carbon Nanotubes

Adedeji E. Agboola and Ralph W. Pike
Louisiana State University

Helen H. Lou, Jack R. Hopper and Carl L. Yaws
Lamar University

Thomas A. Hertwig
Mosaic Corporation

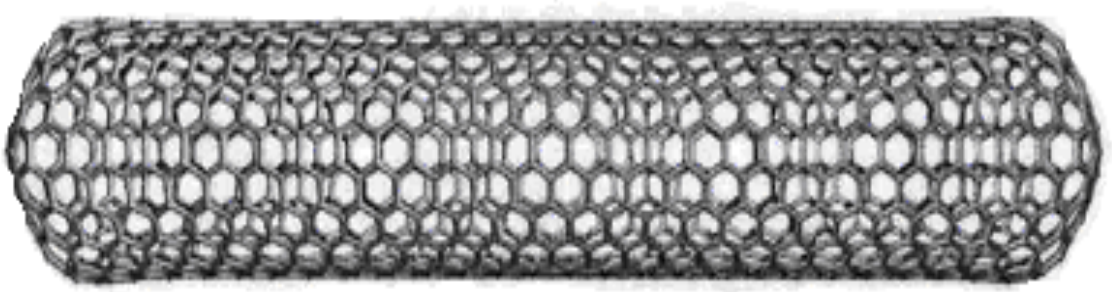
Paper No. 289n, American Institute of Chemical Engineers Annual Meeting,
Cincinnati, Ohio Oct. 30- Nov. 4, 2005

Brief History of Carbon Nanotubes

- Discovered by Iijima and co-workers in 1991

- CNT structures consist of carbon filaments with a small diameter (nm) and a large length (μm)

- A molecular model of a single wall carbon nanotube



Properties

- High Aspect Ratio Structures

- High Mechanical Strength: Tensile Strength (60 GPa) and Young Modulus (1 – 5 TPa)

- High Electrical Conductivity (typically 10^{-6} ohm m)

- High Thermal Conductivity (1750 – 5800 W/mK)

- High Current Density (10^{7} – 10^{9} A/cm^{2})

- Chemical Stability: (not attacked by strong acids/alkali)

Nanotube Composites

- Ideal substitutes to carbon fibers as reinforcements in high strength, low weight and high performance composites

- Application in aerospace construction

Characteristics	Carbon Fibers	Carbon Nanotubes
Diameter	μm	nm
Strength	Low	High
Stiffness	Low	High
Density	High	Low
Conductivity	Low	High

Carbon Nanotube Laboratory Synthesis Techniques

	Arc Discharge	Laser Ablation	CVD
Carbon Source	Graphite	Graphite	Hydrocarbon, CO
Energy Source	Electricity	Laser	Plasma, Furnace
Growth Temp	2500 – 3000 ^{o}C	1,200 ^{o}C	750 – 1100 ^{o}C
Yield	30 % by weight	Up to 70 %	20 % - 100 %
Scalability	Non – scalable	Non – scalable	Scalable
Advantages	- Few or no structural defects	- Diameter control - Few Defects	- Low Temp - Long Length - Diameter Control
Limitations	- High Temp - Short Tubes	- Costly - High power - Expensive laser	- High Defects - Low Crystallinity

Summary of Conceptual Designs of CNT Processes

	CNT PFR Process	CNT-FBR Process
Catalyst	Fe	Co – Mo
	$Fe(CO)_5 \rightarrow Fe + 5CO$	Silica
Reactants	CO and $Fe(CO)_5$	CO
Reactor Type	Plug Flow Reactor	Fluidized Bed
Reactor Conditions	1050 ^oC @ 450 psi	950 ^oC @ 150 psi
Selectivity to CNT	90%	80%
Purification	- Oxidation	- Leaching
	- Acid Treatment	- Froth Flotation
	- Filtration	- Acid Treatment
Production rate (kg/ hr)	595	595

Process Units

Section	CNT-PFR Process	CNT-FBR Process
Feed Preparation	- Mixer, Heater - Gas Compressor	- Mixer/Heater - Gas Compressor
Reaction	- Flow Reactor - Heat Exchangers	- Fluidized Bed - Heat Exchangers
Purification	- Filters - Oxidizer - Drier/Annealer - Centrifuge	- Filters - Flotation Column - Drier/Annealer - Cyclone Separator
CO Recycle	- Gas Absorber - Gas Stripper	- Gas Absorber - Gas Stripper

CNT-PFR Process

Reactants, Product and Emissions

Feed	kg/hr	Other	kg/hr	Product	kg/hr	Emissions	kg/hr
CO	2,637	O_2	253	CNT	595	$FeCl_2$	0.07
$Fe(CO_5)$	627	H_2O	255			CO_2	2,666
						Fe_2O_3	256
						H_2O	255
Total Mass Flow		3,772 kg/hr		Total Mass Flow		3,772 kg/hr	

Energy Requirements

Steam	Natural Gas	Electricity
12,000 kg/hr	486 kg/hr	1,056 kW

CNT-FBR Process

Reactants, Product and Emission

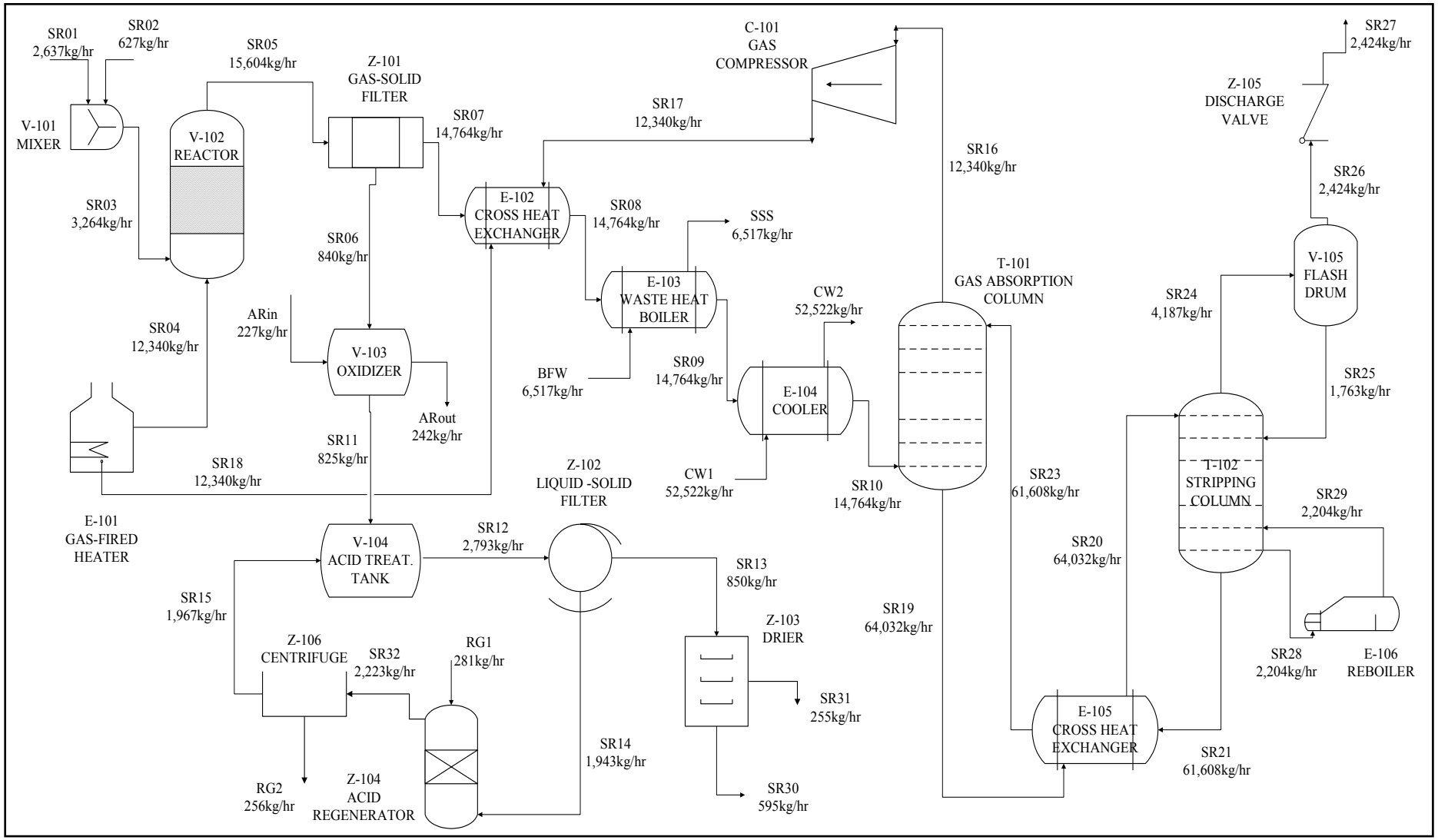
Feed	kg/hr	Others	kg/hr	Product	kg/hr	Emissions	kg/hr
CO	3,471	O_2	9	CNT	595	CO_2	2,727
Mo	19	H_2O	488	$CoCl_2$	0.05	Co_2O_3	26
Co	19	NaOH	228	$MoCl_2$	0.04	MoO_3	28
				H_2O	255	NaOH	228
				H_2	25	CO	349
Total Mass Flow		4,234 kg/hr		Total Mass Flow		4,324 kg/hr	

Energy Requirements

Steam	Natural Gas	Electricity
14,000 kg/hr	486 kg/hr	387 kW

	CNT-PFR Process	CNT-FBR Process
Production Rate	5,000,000 kg/yr	5,000,000 kg/yr
Total Plant Cost	$4.6 million	$4.4 million
Total Product Cost	$186 million	$124 million
Market Price of Carbon Fiber	$90 per kg	$90 per kg
Annual Revenue	$450 million	$450 million
Economic Price	$38 per kg	$25 per kg
Net Present Value	$609 million	$753 million
Rate of Return	37.4%	48.2%

CNT Process using Fluidized Bed Reactor



CNT Process using Plug Flow Reactor