

Environmental Impact Assessment for Potential Continuous Processes for the Production of Carbon Nanotubes

¹Aditi Singh, ¹Helen H. Lou, ²Ralph W. Pike, ²Adedeji Agboola, ¹Xiang Li

¹Jack R. Hopper and ¹Carl L. Yaws

¹Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont, TX 77710

²Department of Chemical Engineering, Louisiana State University
110 Chemical Engineering Bldg., Baton Rouge LA 70803

Abstract: As an emerging discipline, nanotechnology has the potential to improve environmental sustainability through its application in pollution prevention, treatment, remediation, etc. One challenging issue in the growth of nanotechnology is how to produce purified carbon nanotubes (CNT) in commercial quantities at affordable price and with low environmental impacts. A detailed assessment of such a manufacturing process from both economic and environmental aspects at the design phase will benefit both the industry and the society. In this work, an LCA type of environmental impact assessment is conducted for the conceptual design of two catalytic, chemical vapor deposition processes (CNT-PFR and CNT-FBR) used for continuous large-scale production of CNT. The core of both processes is a high-temperature catalytic reactor. Mineral acids are used in the purification steps, from which liquid and solid wastes are generated and must be treated before discharge. Based on the simulation results, the environmental impacts of each process are calculated. The results provide vital information that can be used during the design phase of these processes for better decision-making.

Key words: LCA, carbon nanotube, process design, environmental impacts

INTRODUCTION

Carbon nano-tubes (CNT) are single atom layers of carbon rolled up into tubes with nano-scale diameter. They have wide variety of applications ranging from manufacturing composite fibers for better thermal, electrical and mechanical properties to several varied applications in electronics and optics^[1].

Popular techniques used to manufacture CNT include arc-discharge, laser ablation, using high pressure carbon monoxide and chemical vapor deposition. An extensive literature review was conducted by Agboola^[1], which included information about the reactor type, dimensions, energy requirements, operating conditions, reactants, products, catalysts, conversion, carbon nanotube yield, selectivity as well as purification techniques employed in experimental studies for each process. The candidate production processes were selected from these processes for further analysis on the basis of their capital and operating cost, raw materials selection, operation mode, production/purification methods, and process operating conditions. The details of this selection process can be found in Agboola, 2005^[1].

On the basis of this criteria, two processes were selected to conduct an environmental assessment, the high-pressure carbon monoxide disproportionation in a plug-flow reactor (CNT-PFR) and the cobalt-molybdenum fluidized bed catalytic reactor (CNT-FBR) were selected for the conceptual design. The CNT-PFR reactor has catalytic particles formed *in situ* by thermal decomposition of iron carbonyl. The CNT-FBR process employs the synergistic effect between the cobalt and molybdenum to give high selectivity to carbon nanotubes from CO disproportionation.

In this work, an environmental impact analysis has been conducted to assess the performance of CNT-PFR process and CNT-FBR process in terms of their environmental sustainability. These results are expected to provide the manufacturer with more comprehensive data about each process for better decision-making. In this study, firstly details of the CNT-PFR process and CNT-FBR process are presented. After that, the natural resource consumption and output data for both these processes is discussed. Then, the impact assessment methodology is discussed followed by the results of the case study developed for the CNT-PFR and CNT-FBR processes.

Corresponding Author: Helen H. Lou, Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont TX 77710, Tel 409-880-8207; Fax: 409-880-2197

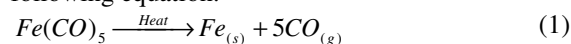
Conceptual design of the CNT-PFR (HiPCO)

process: This design is based on the high-pressure plug flow (PFR) reactor which converts carbon monoxide into single-wall carbon nanotubes and carbon dioxide, at high pressures (30–50 bar), and at temperatures between 1,273 K and 1,473 K from carbon monoxide and iron pentacarbonyl catalyst precursor. The overall conversion of carbon monoxide to carbon nanotubes in the CNT-PFR reactor was 20 mol%^[2]. The process flow diagram for this process is illustrated in Fig. 1. The mass flow rates given in the diagram are in kg/hr. A detailed description of each process unit can be found in Agboola, 2005^[1].

The CNT-PFR process for carbon nanotubes production can be divided into four sections: feed preparation section, the reactor section, the separation/purification section and the absorber section. Next, a brief description of each section is given.

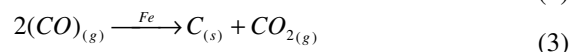
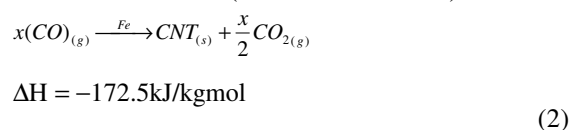
Feed preparation section: The process equipment used in this section includes a mixer (V-101), a gas-fired heater (E-101) and a gas compressor (C-101). The gas streams entering the mixer consist of fresh carbon monoxide (CO) at mass flow rate of 2,637 kg/hr and iron pentacarbonyl vapor (Fe(CO)₅) at 627 kg/hr. The mixer blends them together at 303 K. The gas stream leaving the mixer is sent to the flow reactor (V-102) at 303 K and atmospheric pressure. The unconverted CO is completely recovered and recycled back in the reactor from the compressor. The CO recycle stream passes through two heat exchanger units successively, the cross heat exchanger and the gas-fired heater which increases its temperature to 1,323 K, the required feed temperature for the reactor.

Reactor section: The process units used in this section include a high-pressure reactor (V-102), a gas-solid filter (Z-101), the reactor effluent-feed recycle cross heat exchanger (E-102), the waste heat boiler (E-103), and the heat exchanger water cooler (E-104). The mixed gas stream containing CO saturated with iron pentacarbonyl vapor, and the CO recycle stream from the heater are passed through the flow reactor (V-102). The flow reactor is modeled as an isothermal plug-flow reactor at 450 psia and 1,323 K, based on laboratory experiments^[3]. Upon heating, the iron pentacarbonyl vapor decomposes to iron atoms and CO according to following equation:



The iron formed from the decomposition of the iron pentacarbonyl, nucleates and forms iron clusters that initiate the growth of carbon nanotubes in the gas

phase by carbon monoxide disproportionation exothermic reaction (Boudouard reaction):



In this design, the conversion of CO in the flow reactor to form carbon nanotube is 20 mol%, based on the optimal conversion obtained in the laboratory-scale HiPCO reactor^[4]. The selectivity of CO forming carbon nanotubes is 90% and the selectivity of CO forming amorphous carbon is 10%, based on high TEM studies^[2]. The effluent stream from the reactor contains carbon nanotube (CNT), amorphous carbon, iron particles, CO₂ and unconverted CO. This stream is sent to a gas-solid filter which separates the solid products containing carbon nanotube, residual iron and amorphous carbon from the hot, mixed carbon monoxide and carbon dioxide gas stream. The hot mixed-gas stream is used to preheat the CO recycle stream in the cross heat exchanger. It is then passed to the waste heat boiler that cools the mixed gas stream while producing saturated steam from boiler feed water (BFW). The gas stream is further cooled using cooling water and fed into the gas absorption column (T-101) as bottoms at 330 K.

Separation/purification section: The process units used in the separation/purification section include the previously described gas-solid filter (Z-101), an air oxidizer (V-103), an acid treatment tank (V-104), a liquid-solid filter (Z-102), a product drier (Z-103), an acid regeneration column (Z-104) and a centrifuge separator (Z-106). These process units are used to separate and purify the carbon nanotube product from impurities such as amorphous carbon and iron nanoparticles. The purification process in the CNT-PFR process involves a multi-step approach: oxidation, acid treatment, filtration and drying. In the oxidizer, hot air gas stream is passed over the carbon nanotube product collected from the filter to selectively remove amorphous carbon impurities and oxidize the iron particles to iron oxide^[5]. The oxidized carbon nanotube product containing iron oxides is treated with 12% hydrochloric acid (HCl) solution in the acid treatment tank^[6]. This removes the remaining iron particles embedded in nanotubes in the form of iron (II) chloride (FeCl₂). The final carbon nanotube product contains 97 mol% carbon nanotubes and 3 mol% iron^[2]. The nanotube slurry, containing the dissolved iron chloride, and carbon nanotube is sent to the liquid-solid filter,

which separates the purified carbon nanotubes from the iron chloride solution. The carbon nanotubes collected are washed several times with deionized water and then filtered, purified and dried in the product drier. The iron chloride solution is sent to an acid regeneration column where the hydrochloric acid solution is regenerated.

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 absorption column. The unconverted CO is recovered and recycled back to the reactor. The CO₂-rich MEA solution leaves the gas absorption column from the bottom and enters the solute rich-lean solvent cross heat exchanger which preheats the CO₂-rich MEA solution. Carbon dioxide gas is stripped from the solute-rich MEA solution in the column by steam stripping. The gas stripped from the stripping column is sent to the flash drum, where the carbon dioxide gas stream and water vapor are separated.

Natural resource consumption data for CNT-PFR process: This section provides the natural resource consumption data for CNT-PFR process. It is expressed in terms of total amount of natural gas, water, air and coal consumed for the production of 595 kg/hr of 97 mol % pure CNT.

Water: The total amount of water used in the CNT-PFR process is in form of raw material in acid regeneration column (Z-104) and utilities (CW, BFW and Steam). The HP steam is used in kettle-reboiler (E-106), reactor (V-102) and the product drier (Z-103). The total amount of HP Steam consumed is 4439 kg/hr. Apart from this, water is also used for cooling in the form of cooling water and boiler feed water (E-104, V-103, E-103). This adds up to 59545 kg/hr of water. Water is also used in the acid regeneration column at the rate of 255 kg/hr. This adds up to a total consumption of 64239 kg of water per hour. The details of total water consumption are tabulated in Table 1.

Natural gas: Natural gas is used to heat the gas fired heater (E-101). It is also assumed to be used as fuel for producing HP steam, and for providing 809288 kJ/hr to the gas stripping column (T-102). In order to calculate the total consumption of natural gas, it is assumed that

Table 1: Total water consumed in CNT-PFR process

Unit	Material	Flow Rate (Kg/hr)
E-103	BFW	6517
E-104	CW	52522
V-103	CW	506
E-106	HP Steam	2565
V-102	HP Steam	1482
Z-103	HP Steam	392
Z-104	H2O	255
	Total Water	64239

Table 2: Total amount of natural gas consumed for HP steam production in CNT-PFR process

Unit	Material	Flow Rate (Kg/hr)	Heat Provided (Kj/hr)
E-106	HP Steam	2565	4261155
V-102	HP Steam	1482	2462606
Z-103	HP Steam	392	650984
	Net HP	4439	7374745
	Equipment Efficiency (75%)		9832993
	Boiler Efficiency (65%)		15127682
	NG Used (kg/hr)		272.56

Table 3: Total natural gas consumed in CNT-PFR process

Unit	Material	Flow Rate (Kg/hr)
E-101	NG	486
E-106	HP Steam	
V-102	HP Steam	
Z-103	HP Steam	272.56
T-102	NG	19.44
	Total NG Used	778

Table 4: Total amount of air consumed in CNT-PFR process

Unit	Material	Flow Rate (Kg/hr)
V-103	O ₂	176
Z-104	O ₂	26
	Total O ₂	202
	Total Air	1058

the heat transfer efficiency of each equipment is 75% and the heat transfer efficiency of the boiler used for steam production is 65%. A back calculation gives the total amount of natural gas used for the production of HP steam as 272.56 kg/hr (Table 2). The total amount of natural gas used in the CNT -PFR process is 778 kg/hr (Table 3). The value of heat of combustion of natural gas used for these calculations is 55501.2 kJ/hr.

Air: Air is consumed directly in air oxidizer (V-103) as a source of oxygen. Moreover, the acid regeneration tank also uses some oxygen. Although both streams contain 100% oxygen, it is assumed that this oxygen is obtained from air and air is used 10% in excess. Thus, a back calculation by assuming air has 21% oxygen gives the total amount of air used as 1058 kg/hr (Table 4).

Coal: The gas compressor (C-101) uses 1056 kW of electricity. It is assumed that the fuel used for the production of electricity is coal. Using the conversion

Table 5: Total carbon dioxide produced by CNT-PFR process

Stream	Components	Flow Rate (kg/hr)
ARout	CO ₂	242
SR27	CO ₂	2424
	Total CO ₂	2666

Table 6: Total water consumed in CNT-FBR process

Total Water Consumption		
Unit	Material	Flow Rate (Kg/hr)
Z-207	HP Steam	223
V-201	HP Steam	2168
Z-206	HP Steam	392
E-205	HP Steam	2885
Z-208	H ₂ O (l)	265
E-202	BFW	59089
E-203	CW5	7333
	Total Water	72355

factor (1 kW-h of electricity = 10000 Btu fuel in power plant), the total amount of coal used on an hourly basis for providing power to the compressor is calculated as 40.109×10^6 MJ.

Emissions/discharge data for CNT-PFR process:

The CNT-PFR process produces carbon nanotubes with trace amounts of iron (II) chloride (FeCl₂) as impurity. This impurity is treated as a part of the final product. Since the scope of the impact assessment conducted in this study is only from “Entry-to-Exit”, it does not include the usage and disposal phase of the carbon nanotubes produced by CNT-PFR process. Due to this, the FeCl₂ in the CNT is treated as a part of the final saleable product. Apart from these, the process produces carbon dioxide, water and iron (III) oxide. This section provides a brief description about these emissions. Since the scope of this study is “Entry-to-Exit”, we do not treat FeCl₂ as an emission to the environment. It is treated as a part of the final saleable product. Other chemicals emitted from the process are listed below.

Carbon dioxide (CO₂): Total CO₂ released by CNT-PFR process is 2666 kg/hr (Table 5). When released in the atmosphere, pure CO₂ traps outgoing long wave radiation and adds to global warming. This pure carbon dioxide generated by CNT-PFR process can be used as a raw material for other processes^[7]. Thus, this carbon dioxide may either be released in the atmosphere as it is or can be reused as a resource by another process.

Ferric oxide (Fe₂O₃): The centrifuge (Z-106) produces 256 kg/hr of Fe₂O₃. It is a reddish-brown powder which has less than 1% solubility in water. This can be either disposed in a land-fill site or sold as a by product to be used as a raw material. Fe₂O₃ can be used for

Table 7: Total natural gas consumed in CNT-FBR process for HP steam production

Unit	Flow Rate (kg/hr)	Heat provided (Kj/hr)
V-201	HP Steam	2168
Z-206	HP Steam	392
E-205	HP Steam	2885
Z-207	HP Steam	223
	Net HP	5668
	Equipment Efficiency (75%)	12555247
	Boiler Efficiency (65%)	19315764
	NG Used (kg/hr)	348.02

Table 8: Total natural gas consumed in CNT-FBR process

Unit	Material	Flow Rate(Kg/hr)
E-201	NG	616
V-201	HP Steam	
Z-207	HP Steam	
Z-206	HP Steam	
E-205	HP Steam	348.02
T-202	NG	16.40
	Total NG Used	980.42

production of pure iron or as pigment for coloring in cosmetics and ceramic^[8]. The OSHA Permissible Exposure Limit (PEL) for Iron oxide fume is 10 mg/m³.

Water (H₂O): The total amount of water released in this process depends upon how much water is being recycled. We can consider two different scenarios for this. In the first case, no water stream is recycled and all the water needs to be sent to a treatment facility before reuse. In that case the net output of water will be the same as input, 64239 kg/hr. Another possibility is that all the water is recycled. Since the water coming out of the product drier (Z-103) is pure, even that is recycled back to the acid-regeneration column. In this case, the amount of water dumped would be 0 kg/hr. This however, does not account for water losses of any kind during the steam cycle or in any other equipment.

Conceptual design of the CNT-FBR process: This design is based on carbon monoxide disproportionation over silica supported cobalt–molybdenum catalyst in a fluidized bed reactor. The reaction forms carbon nanotubes and carbon dioxide at temperatures between 973 K and 1,223 K, and total pressure ranges from 15 psia to 150 psia. The conversion of CO in this process is 20 mol% and its selectivity is 80%^[9]. The process flow diagram for the CNT-FBR process is shown in Fig. 2 where all the mass flow rates are in kg/hr. A detailed description of each process unit can be found in Agboola, 2005^[1]. The CNT-FBR process consists of the four sections: the feed preparation section, the reactor section, the absorber section and the separation/purification section. Next, a brief description of each section is provided.

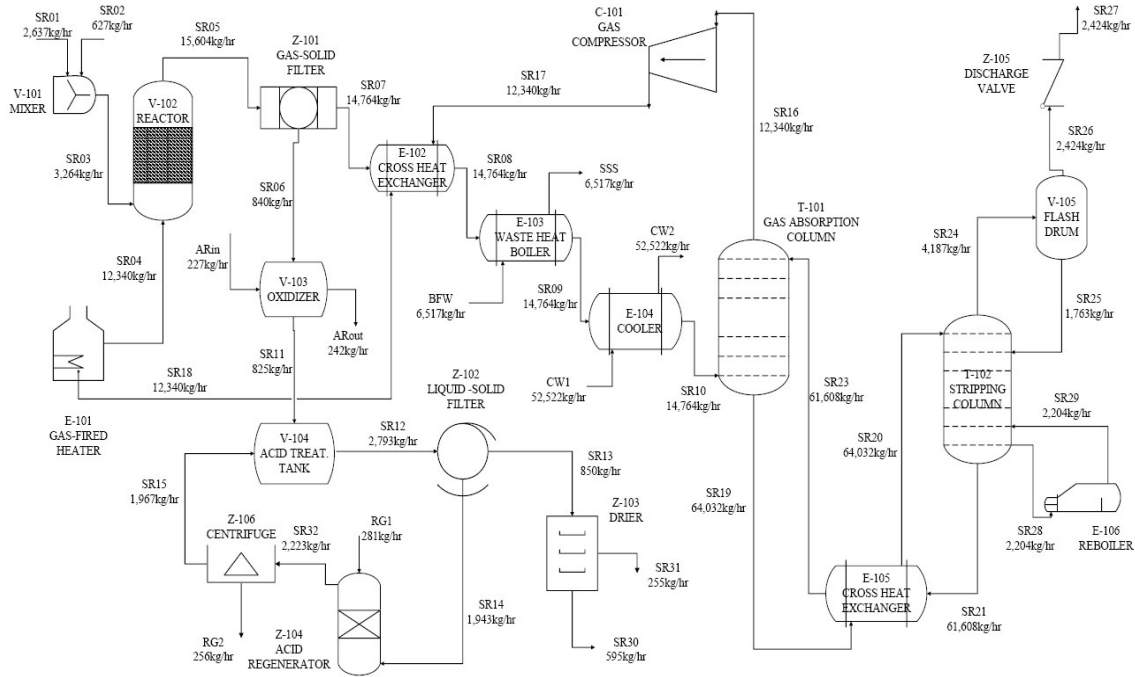


Fig.1: Process flow diagram for the CNT-PFR carbon nanot

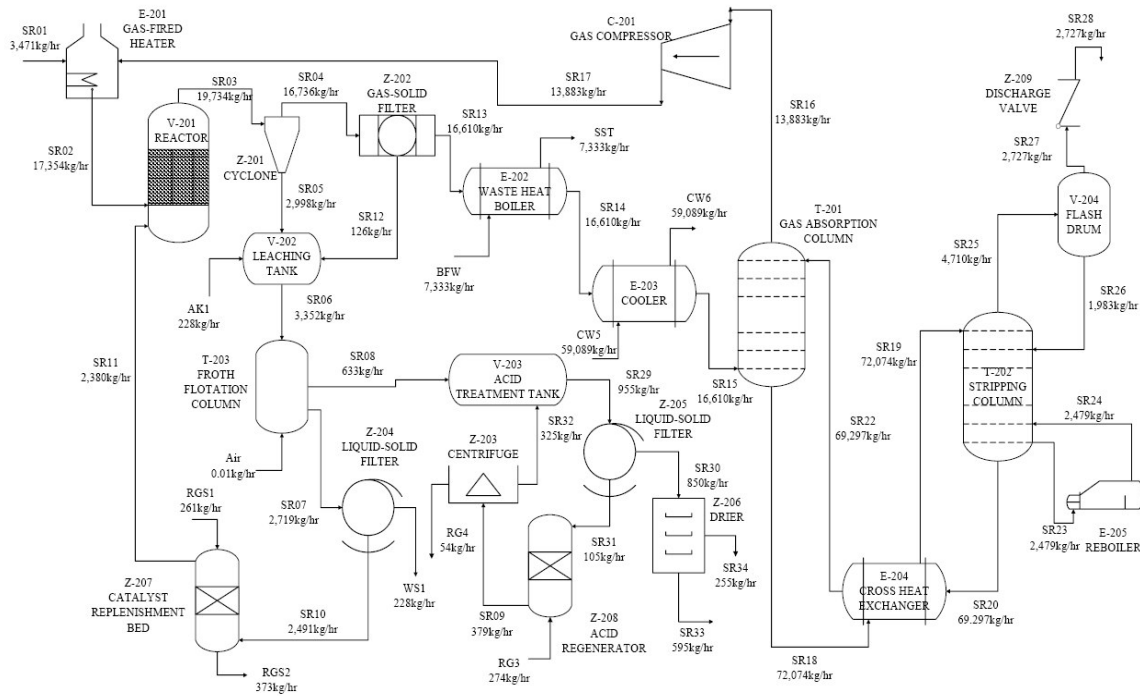


Fig. 2: Process flow diagram for the CNT-FBR carbon nanotube production process

Feed preparation section: The process units in the feed preparation section include the heater (E-201) and the gas compressor (C-201). The fresh feed of CO is combined with the CO recycle stream in the gas-fired heater. The combined CO feed stream is fed into the fluidized bed reactor at 1,223 K and 150 psia. The operating conditions in the reactor are maintained at 1,223 K and 150 psia, based on the experimental conditions in the laboratory-scale CNT-FBR process.

Reactor section: The reactor section consists of a fluidized bed reactor (V-201), the cyclone separator (Z-201), the gas-solid filter (Z-202), the waste heat boiler (E-202) and the heat exchanger water cooler (E-203). In the fluidized bed reactor, the CO feed stream is reacted on silica-supported cobalt-molybdenum catalysts at 1,223 K and 150 psia. Carbon nanotubes are formed by CO disproportionation over Co-Mo catalysts, according to the Boudouard reaction. The conversion of CO in the fluidized bed reactor to form carbon nanotube is 20 mol%. The selectivity of carbon monoxide to form carbon nanotubes with this reaction is 80% and to form amorphous carbon is 20%. The effluent stream from the reactor contains carbon nanotubes, amorphous carbon, carbon dioxide and unconverted carbon monoxide. It is passed through a cyclone separator to separate the solid catalyst particles from the hot mixed-gas stream. The gas stream from the cyclone is passed through a gas-solid filter to remove any solid catalyst entrainments. The entrained solids are sent to the alkali leaching tank. The hot gas stream from the gas-solid filter is sent through a waste heat boiler which cools the mixed-gas stream while converting boiler feed water to saturated steam. The mixed-gas stream leaving the waste heat boiler is further cooled to 330 K using cooling water.

Separation/purification section: The carbon nanotubes produced in the fluidized bed reactor are grown on and remain attached to the silica-supported bimetallic catalysts. Froth flotation purification process is used to separate and purify the carbon nanotube using air as an inorganic solvent. The purity of carbon nanotubes produced by the froth flotation process is only 80%^[10]. Next, they are dissolved in 12% hydrochloric acid (HCl) solution which improves the purity of the final nanotube product to 97 mol% CNT^[9]. The silica-supported solid catalyst from the cyclone separator is sent to the alkali leaching tank, where it is washed with 2M sodium hydroxide solution. This solution breaks the carbon nanotubes-supported

catalysts interaction by silica leaching without removing the cobalt-molybdenum metals present on the silica substrate. In the acid treatment tank, the residual cobalt and molybdenum catalysts react with hydrochloric acid solution to form soluble cobalt chloride and molybdenum chloride respectively. The carbon nanotube slurry is then passed through a liquid-solid filter which separates the purified carbon nanotube product from the liquid stream. The purity of the final carbon nanotubes product, obtained after acid dissolution and filtration, is 97 mol% carbon nanotubes, 1.5 mol% cobalt metal and 1.5 mol% molybdenum metal particles^[9]. The hydrochloric acid is recovered in an acid regeneration column from the oxidation of metal chlorides solution. The cobalt and molybdenum oxides produced in the acid regenerator are removed from the hydrochloric acid in the centrifuge separator. The recovered acid solution is subsequently recycled to the acid treatment tank.

Absorber section: After cooling, the outlet stream is sent to the absorber. The carbon dioxide in the feed is absorbed in the counter-current flow of MEA solution fed at the top of the absorption column. The unconverted CO gas stream is recycled to the reactor. The solute-rich MEA solution leaving the gas absorber at the bottom is passed to the solute-rich-lean solvent cross heat exchanger, where it is preheated by the lean MEA solution recovered from the stripping column in a cross heat exchanger. Carbon dioxide gas is stripped from the solute-rich solution in the gas stripper using saturated steam. The carbon dioxide leaves the stripping column from the top and is sent to the flash drum where any entrained liquid is recovered and returned to the gas stripping column.

Natural resource consumption data for CNT-FBR process: The following section presents the natural resource consumption data for CNT-FBR process. They are presented in terms of total water, natural gas, air and coal consumption.

Water: The total amount of water consumed in CNT-FBR process is in the form of raw material in acid regeneration column (Z-208) and utilities (CW, BFW and Steam). The total amount of water used for the production of HP steam used in kettle reboiler (E-205), reactor (V-201), the product drier (Z-206) and catalyst regeneration bed (Z-207) is 5668 kg/hr. Apart from this, 265 kg/hr of fresh water is used in acid regeneration column (Z-208). Moreover, 59089 kg/hr of boiler feed

water is used in waste heat boiler (E-202) and 7333 kg/hr of cooling water is used in heat exchanger water cooler (E-203). All these adds to a total consumption of 72355 kg/hr of water (Table 6).

Natural gas: In the CNT-FBR process natural gas is used to heat the gas fired heater (E-201). It is assumed that natural gas is also used to produce the HP steam used in the process. Similar to CNT-PFR process, the heat transfer efficiency of each equipment is assumed to be 75% and that of a boiler is assumed to be 65%. Using this data, it was found that the total amount of natural gas used for production of HP steam is 348.02 kg/hr (Table7). The source of heat used to provide 910268 kJ/hr of heat to the gas stripping column (T-202) is assumed to be natural gas. A back calculation shows that the total amount of natural gas used in the CNT-FBR process is 980.42 Kg/hr (Table 8). The value of heat of combustion of natural gas used for these calculations is 55501.2 kJ/hr.

Air: Air is consumed directly in froth flotation column (T-203) as an inorganic solvent and in acid regeneration column (Z-208) as a source of oxygen. It is assumed that air is used 10% in excess. With these assumptions, the total amount of air used is found to be 47.15 kg/hr (Table 9).

Coal: The gas compressor (C-101) uses 387 kW of power. It is assumed that the fuel used for production of electricity is coal. Using the conversion factor (1 kW-h of electricity = 10000 Btu fuel in power plant), the total amount of coal used on an hourly basis was calculated to be 14.69×10^6 MJ. Thus to provide 387 kW power for the compressor, the total amount of coal used on an hourly basis is 14.69×10^6 MJ.

Emissions/discharge data for CNT-FBR process: The carbon nanotubes produced by CNT-FBR process contain trace amounts of cobalt (II) chloride (CoCl₂) and molybdenum (II) chloride (MoCl₂) as impurity. In this study, we do not account for the entire life cycle of the carbon nanotubes. The scope of this study is from "Entry-to-Exit" for the particular process flow sheet in discussion. This does not include the usage and disposal phase of the products. Due to this, the impurities in the product are treated as a part of the final saleable product. However, the CNT-FBR process produces several other chemicals which include carbon dioxide, carbon monoxide, water, sodium hydroxide (NaOH), cobalt (III) oxide (Co₂O₃) and molybdenum oxide (MoO₃). In this section the detail of non-product

Table 9: Total air consumed in CNT-FBR process

Air Consumption		
Unit	Material	Flow Rate (Kg/hr)
T-203	Air	0.01
Z-208	O ₂	47.14
	Total Air	47.15

Table 10: Input data for base case of CNT-PFR and CNT-FBR process

CNT-PFR Process		CNT-FBR Process	
Component	Flow Rate (kg/hr)	Component	Flow Rate (kg/hr)
Air	1058	Air	47.15
Water	64239	Water	72355
Component	Flow Rate (kj/hr)	Component	Flow Rate (kj/hr)
Natural Gas	778	Natural Gas	980.42
Coal	4.01E+10	Coal	1.47E+10

Table 11: Output data for base case of CNT-PFR and CNT-FBR process

CNT-PFR Process			CNT-FBR Process		
Component	Flow Rate (kg/hr)	Media of Disposal	Component	Flow Rate (kg/hr)	Media of Disposal
CO ₂	2666	Air	CO ₂	2727	Air
H ₂ O	64239	Water	H ₂ O	72355	Water
Fe ₂ O ₃	256	Soil	Co ₂ O ₃	26	Air
			MoO ₃	28	Air
			NaOH	228	Soil
			CO	349	Air
			H ₂	25	Air

outputs of CNT-FBR process are discussed. These include:

Carbon dioxide (CO₂): The total amount of CO₂ released by CNT-FBR process is 2727 kg/hr by discharge valve (Z-209). This pure CO₂ can be either released in the atmosphere or reused as a byproduct to be used as raw material for any economic process^[7].

Carbon monoxide (CO): The catalyst regeneration bed produces 349 kg/hr of CO. It can have serious health impacts on humans when exposed to levels of 200 ppm or higher for a long time. It may also contribute to global warming. On the other hand, it can be used for the production of methanol, aldehydes etc. Thus, CO can either be released in the atmosphere or reused as a raw material either in the same process or any other process^[11].

Water (H₂O): The total amount of water released depends upon various scenarios discussed previously. If all the water is recycled, the net disposal would be zero. However, if nothing is recycled and is sent to the treatment facility then the net water discharged would be 72355 kg/hr.

Cobalt (III) oxide (Co₂O₃): The Centrifuge Separator (Z-203) produces 26 kg/hr of Cobalt(III) Oxide. It is a non combustible black-grey crystalline powder which

Table 12: Environmental impact data for base design of CNT-PFR and CNT-FBR Process

Impact category	Unit	CNT-PFR Process	CNT-FBR Process
Global Warming	CO ₂ eq.	6.29	5.82
Acidification	H+ moles eq.	0.1570	0.0799
HH Noncancer	toluene eq.	0.0583	0.0695
Smog	NOx eq.	0.00252	0.00939
HH Criteria Air-Mobile	PM2.5 eq.	0.000421	0.000182
HH Criteria Air-Point Source	PM2.5 eq.	0.00040	0.00017
Eutrophication	N eq.	0.000102	0.0000621
HH Cancer	benzene eq.	0.0000559	0.0000644
Ecotoxicity	2,4-D eq.	0.0000373	0.0000137

Table 13: Environmental impact data for new design

Impact category	Unit	CNT-PFR Process	CNT-FBR Process
Global Warming	CO ₂ eq.	1.81	1.24
Acidification	H+ moles eq.	0.157	0.0799
HH Cancer	benzene eq.	0.0000559	0.0000644
HH Noncancer	toluene eq.	0.0583	0.0695
HH Criteria Air-Point Source	PM2.5 eq.	0.00040	0.00017
HH Criteria Air-Mobile	PM2.5 eq.	0.000421	0.000182
Eutrophication	N eq.	0.0001020	0.0000621
Ecotoxicity	2,4-D eq.	0.0000373	0.0000137
Smog	NOx eq.	0.00252	0.00154

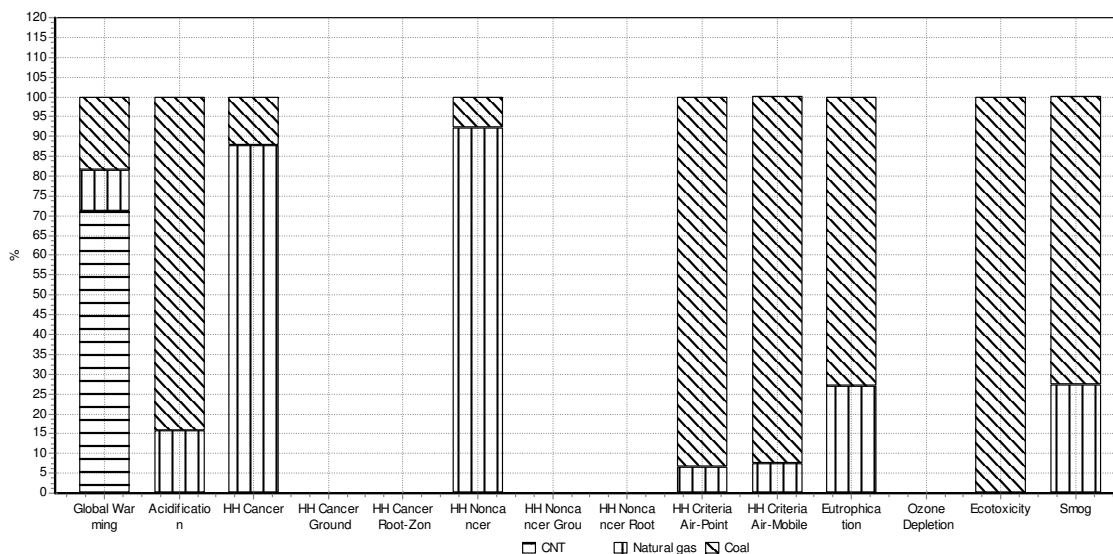


Fig. 3: Environmental impact of CNT-PFR process using base design

causes cough, sore throat and shortness of breath if inhaled. Ingestion may cause abdominal pain or nausea. Its exposure limit is 0.02 mg/m³. Although rigorous studies have not been conducted to check if Co₂O₃ is a human carcinogen, other cobalt compounds have been found to be carcinogenic. Thus, it can be considered as a potential human carcinogen. On the contrary, it can be used in ceramics for coloring or for extracting cobalt. Thus, this Co₂O₃ can be either disposed as a waste or

can be reused as a resource by another process to recover Cobalt or may be used as it is.

Molybdenum oxide (MoO₃): The effluent stream of the centrifuge separator (Z-203) produces 28 kg/hr of molybdenum oxide. It is a white to off white powder and is considered to be a toxic material, which may cause severe distress, cramping, vomiting, and hypertension when taken in large doses. The OSHA Permissible Exposure Limit (PEL) for soluble

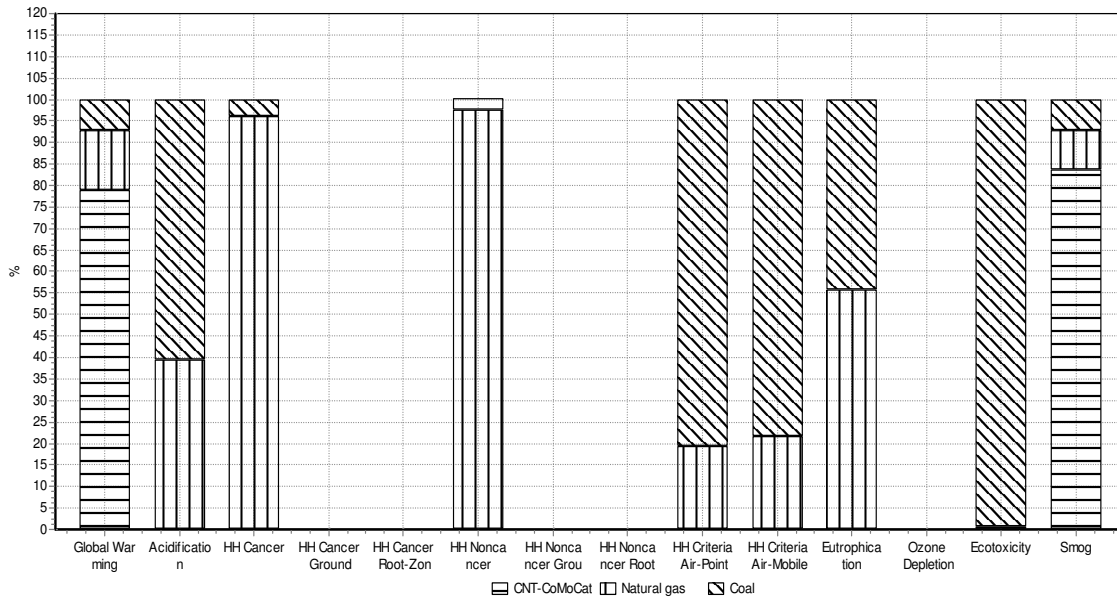


Fig. 4: Environmental impact of CNT-FBR process using base design

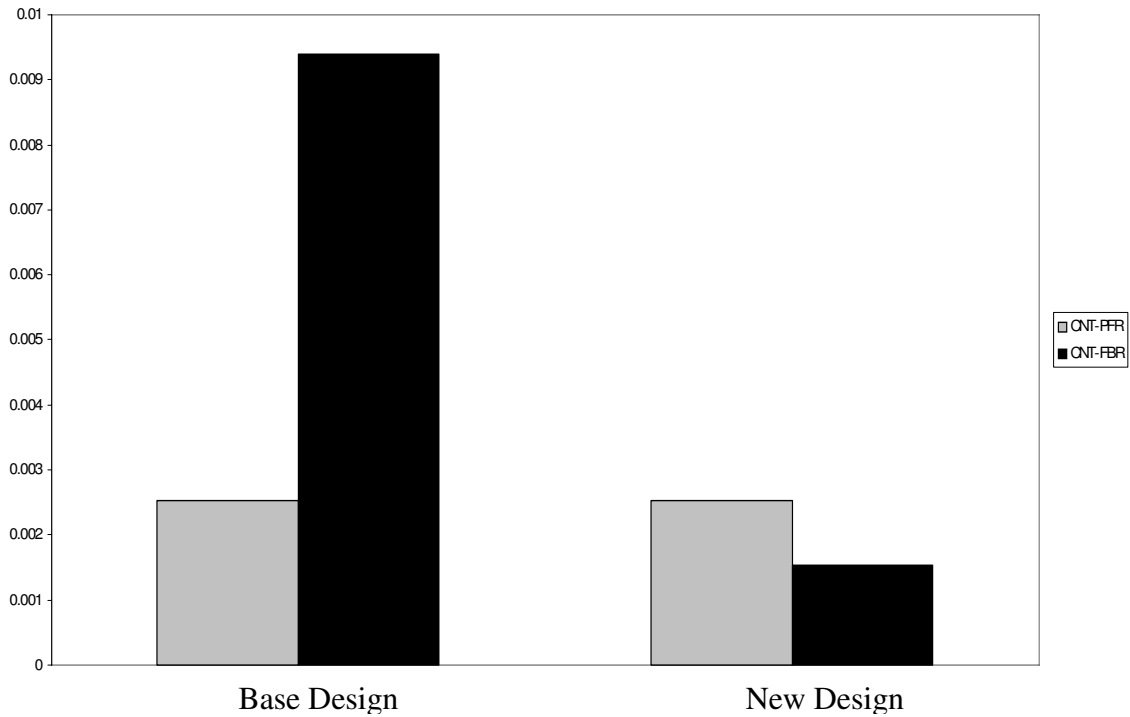


Fig. 5: Contribution of CNT-PFR and CNT-FBR process to smog formation in base design and new design

molybdenum compounds is 5 mg/m^3 and for insoluble molybdenum compounds is 15 mg/m^3 . It is slightly soluble in water. It can be either disposed as a waste or

can be reused as a resource by another process to recover molybdenum or may be used as it is.

Table 14: Contribution of CNT-PFR and CNT-FBR Process to smog formation in base

Design and New Design		
	Base	New
CNT-PFR	0.00252	0.00252
CNT-FBR	0.00939	0.00154

Table 15: Contribution of CNT-PFR and CNT-FBR process to global warming in base

Design and New Design		
	Base	New
CNT-PFR	6.29	1.81
CNT-FBR	5.82	1.24

Sodium hydroxide (NaOH): The liquid-solid filter (Z-204) produces 228 kg/hr of sodium hydroxide. It is a strong base used in the chemical industry. It can be used to drive chemical reactions, neutralize acidic materials, as a neutralizing agent in petroleum refining etc. Sodium hydroxide solutions containing high concentrations of sodium hydroxide may cause chemical burns, permanent injury or scarring, and blindness. It would be best to reuse it for the same process if possible, or treat it as a by product and sell it after necessary treatment.

Hydrogen (H₂): The catalyst regeneration bed (Z-207) produces 25 kg/hr of hydrogen. This comes out in a mixed stream with carbon monoxide. Since there is no toxicity data available for Hydrogen, this hydrogen can be either separated from the mixture or can be reused or disposed in the environment. However, since it is highly combustible, it should be handled with care.

Environmental impact assessment methodology: In order to assess the environmental impacts of these processes TRACI methodology is employed in SimaPro 7.0^[12]. TRACI stands for The Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI) developed by USEPA. It consists of a modular set of impact assessment methods that provide the most up-to-date impact assessment for US based products/processes. It facilitates environmental comparison of products and process alternatives for internal environmental decision-making^[13]. TRACI first classifies the resources and releases into various impact categories and then characterizes them based on the impact categories using their characterization value. The characterization value quantifies the extent of harm that a stressor can cause in a particular impact category^[13]. TRACI characterizes various stressors into the following impact categories:

Ozone depletion: It accounts for the depletion of the protective ozone layer in the earth's stratosphere due to harmful emissions like chlorofluorocarbons, halons, etc. The contribution in this impact category is measured as, Ozone Depletion Index = $\sum_i e_i \times ODP_i$

where, e_i is the emission (in kg) of substance i and ODP_i is the ozone depletion potential of substance i . The ozone depletion index is measured in terms of CFC-11 equivalents / kg emission.

Global warming: It refers to the change in earth's climate due to the build-up of chemicals that trap heat from the sunlight like carbon dioxide, methane, nitrous oxide, etc. The contribution towards global warming is measured as,

$$\text{Global Warming Index} = \sum_i e_i \times GWP_i$$

where e_i is the emission (in kg) of substance i and GWP_i is the global warming potential of substance i . The global warming index is measured in terms of CO₂ equivalent / kg emission.

Acidification: This includes the chemicals that increase the acidity of water and soil systems by releasing [H⁺] or equivalents. TRACI uses the emission data of NO_x and SO₂ for this. The contribution to this impact category is expressed in [H⁺] moles equivalent deposition/ kg emission.

Eutrophication: Eutrophication is a phenomenon in an aquatic ecosystem where high nutrient concentration stimulates algae growth. The contribution in this impact category is measured in terms of nitrogen equivalents released / kg of emission.

Photochemical smog: The characterization value associated with this impact category accounts for the formation of ozone molecules in troposphere which is influenced by the ambient concentrations of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) The contribution in this impact category is measured in terms of NO_x or equivalent.

Human health cancer and non-cancer: This involves reliable ranking and relative comparisons of a large number of chemicals in terms of their potential to cause toxicological impacts. The contribution for Human Health Cancer is measured in terms of benzene equivalents released / kg of emission. The contribution for Human Health Non-Cancer is measured in terms of toluene equivalents released / kg of emission.

Human health criteria: This accounts for measuring the ambient concentrations of particulate matter found to be associated with changes in background rates of chronic and acute respiratory systems as well as the mortality rate. The contribution to this impact category is given in terms of DALYs (Disability Adjusted Life Years) / tonne of emission.

Eco-toxicity: It uses Ecological Toxicity Potential (ETP) to quantitatively measure the ecological harm of a unit quantity of chemical released in the environment. The contribution to this impact category is measured in terms of 2,4-Dichloro-phenoxyacetic acid equivalents released / kg of emission.

Fossil fuel use: The contribution in this impact category is calculated using:

$$\sum_i N_i \times F_i$$

where N_i is the increase in energy input requirements per unit of consumption of fuel i and F_i is the consumption of fuel i per unit of product. The contribution in this impact category is measured in MJ of surplus energy per MJ of extracted energy in the process.

Land use: The contribution in this category is calculated using

$$\text{Land Use Index} = \sum_i A_i \times (T \& E_i) / CA_i$$

where, A_i is the human activity per functional unit of the product, $T \& E_i$ is the T&E species count for the county and CA_i is the area of the county under consideration.

Water use: This impact category captures the significant use of water in areas of low availability. The contribution in this impact category is measured in gallons. TRACI has been developed to provide the most up-to-date possible treatment of impact categories for North America.

In this study, we conduct a comparative environmental impact analysis for two case studies developed for the CNT-PFR process and CNT-FBR process. The first case study – “Base Design” uses the process data as it is. It assumes that there is no recycle or reuse of resources in both these processes. The results for the Base Design are calculated by directly using the input-output data from the flowsheet. The second case study – “New Design” assumes that all the material that is being generated apart from the main product is a by-product and can be used to generate

revenue for each process as it can not only be sold to another manufacturer but also cuts down the disposal/treatment cost or penalty that the company may have to pay.

Case study 1. Environmental impact calculation for base design:

In the base design of the two processes, it is assumed that none of the resources are recycled. All the outputs coming out of the system are treated as emissions. It is assumed that the outlet streams, except the main product stream are disposed to the environment. The natural resource consumption data and the output data for the CNT-PFR process and CNT-FBR process for the base design is presented in Table 10 and 11 respectively. A comprehensive illustration of contribution of CNT-PFR towards each impact category is given in Fig. 3. A similar illustration for CNT-FBR process is given in Fig. 4.

The results generated by using TRACI for the base design are tabulated in Table 12. The contribution of CNT-PFR process towards global warming, acidification, human health criteria (Air: Point Source and Mobile), eutrophication and ecotoxicity is much higher than that of CNT-FBR process. On the other hand, the contribution of CNT-FBR process is higher towards human health non-cancer and smog formation. Thus there is a tradeoff between various categories. However, in terms of base design, the performance of CNT-FBR process is better as its contribution in most of the categories is much lower.

Case study 2. Environmental impact calculation for new design:

The new design scheme is developed based on the principle that no product is waste. All the outlets coming from each process are treated as a by-product. As mentioned previously, each compound can be reused as it is or after processing. Thus it makes no sense to dispose them all into the environment. For both processes, water is recycled. As a result of which, there is not net consumption of water except for the minimal losses. We do not account for that in the current study. The consumption of natural resources remains the same for both processes except for water consumption which is recycled completely.

The environmental impact data for each of these designs is listed in Table 13. A comparison of these impact values shows that the impact of both processes has reduced manifold in terms of contributions towards global warming and smog formation (Tab 14 and 15). Another interesting observation is that the contribution of CNT-PFR process towards smog formation exceeds that of CNT-FBR process in the new design scheme.

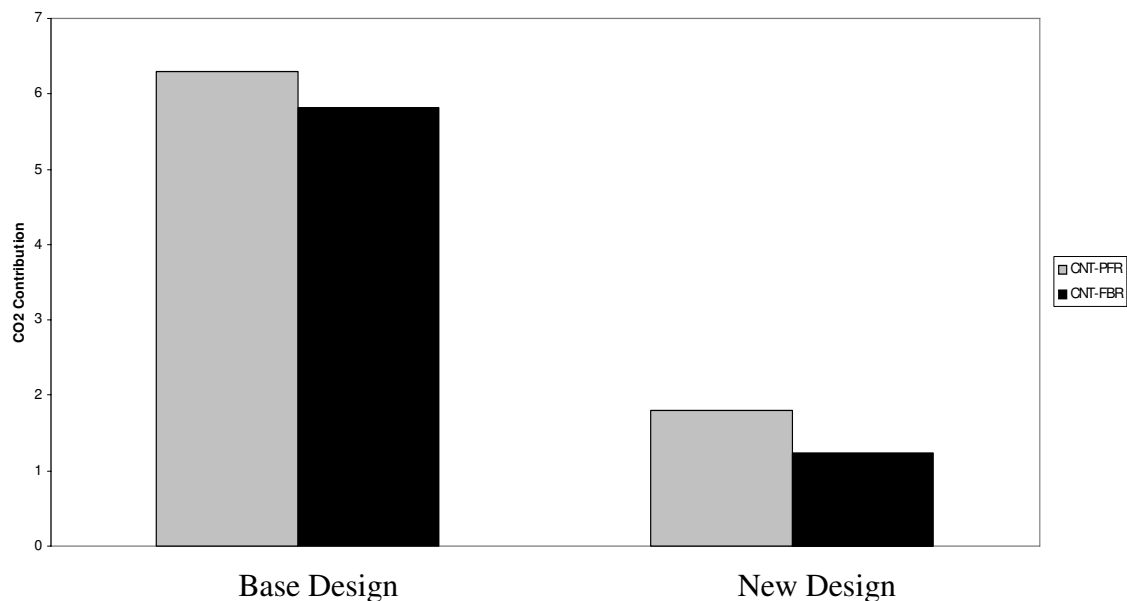


Fig. 6: Contribution of CNT-PFR and CNT-FBR process to global warming in base design and new design

This is illustrated in Fig. 5 and 6. This again proves that depending upon the waste disposal scenario, the performance of each process may change significantly.

DISCUSSION

In this work, an attempt was made to demonstrate the utility of conducting a comprehensive environmental impact assessment of carbon nanotubes production facility. These processes were defined in the software SimaPro 7.0. In SimaPro, each new product/process is defined as a combination of predefined products/processes available in it. For the current case study, we have used the “Carbon Fiber” to represent the carbon nanotubes. This is the product that could most closely represent the carbon nanotubes. The drawback of such an approach is that since it selects a predefined module, it automatically adds the corresponding consumptions and emissions that have been defined for the default process. All the other emissions/consumptions we define are an addition to it. In our case, it does not make much difference because we are doing a comparative analysis. Since we use Carbon Fiber production process as the basis for both CNT-PFR and CNT-FBR process, the default consumptions defined for Carbon Fiber Production process cancel each other.

As shown in the results, the environmental performances of each process may change drastically

depending upon whether the non-product outputs are treated as a by-product or waste. It was observed that from the base design to the new design, the emission of carbon dioxide, carbon monoxide and hydrogen is reduced as we treat them as by-products in new design.

However, another important observation is that the performance of these processes has switched from base design to the new design in terms of its contribution towards smog formation. This shows that a comprehensive environmental impact assessment may produce vital data about the performance of each process in terms of various environmental impact categories. This comes in handy when designing a process for a particular region where one impact category is more crucial than others.

In the input/output data of the CNT-FBR process and CNT-PFR process, it was observed that they generate a lot of unconventional effluents like Fe_2O_3 , Co_2O_3 , MoO_3 , NaOH during the manufacturing phase. Eventually, they may also release FeCl_2 , CoCl_2 and MoCl_2 along with carbon during the usage and disposal phase of CNT. It was found that the available databases in SimaPro could not account for the environmental impact of these chemicals on the environment (emission in air, water or soil). This was mainly due to the lack of characterization values for these particular chemicals for different discharge media. With evolving technologies and upcoming state-of-the-art processes being developed to produce new and better products, it

is required to keep up with the corresponding emissions data in terms of their characterization factors for various discharge media. This is crucial in order to have a better understanding of the short-term as well as long-term impacts of new processes on environmental sustainability.

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REFERENCES

1. Agboola, 2005. Development and Model Formulation of Scalable Carbon Nanotube Processes: HiPCO and CoMoCAT Process Models, M.S. thesis, Louisiana State University, Baton Rouge, LA.
2. Bronikowski, M.J., P.A. Willis, T.D. Colbert, K.A. Smith and R.E. Smalley, 2001. Gas-phase Production of Carbon Single-walled nanotubes from carbon monoxide via the HiPCO Process: A parametric study. *J. Vacuum Sci. Tech. A.*, 19: 1800-1805.
3. Nikolaev, P., 2004. Gas-Phase Production of Single Walled Carbon nanotubes from Carbon Monoxide: A review of the HiPCO Process. *J. Nano Sci. and Nano Tech.*, 4: 307-316.
4. Davis, V.A., 2005. Carbon Nano Tech. Laboratory, Chemical Engineering Department, Rice University. Private Communication.
5. Chiang, I.W., B.E. Brinson, R.E. Smalley, J.L. Margrave and R.H. Hauge, 2001. Purification and Characterization of Single-Wall Carbon Nanotubes. *J. Phys. Chem. B.*, 105: 1157-1161.
6. Meyyappan, W. and D. Srivasta, 2003. Handbook of Nano Sci. Engin. and Tech., 18: 1-26.
7. Xu, A., R.W. Pike, S. Indala, F.C. Knopf, C.L. Yaws and J.R. Hopper, 2005. Development and integration of new processes consuming carbon dioxide in multi-plant chemical complexes. *Clean Technology and Environmental Policy*, 7: 97-115.
8. Greenwood, N.N. and A. Earnshaw, 1984. *Chemistry of the Elements*. Pergamon Press.
9. Resasco, D.E., W.E. Alvarez, F. Pompeo, L. Balzano, J.E. Herrera, B. Kitiyana and A. Borgna, 2001. A scalable process for production of single-walled carbon nanotubes by catalytic disproportionation of CO on a solid catalyst. *J. Nanoparticle Res.*, 00, 1-6.
10. Pisan, C., S. Chavadej, B. Kitiyana, J.F. Scamehorn and D.E. Resasco, 2004. Separation of Single-Wall Carbon Nanotubes from Silica by Froth Flotation Technique AIChE Annual Meeting, Indianapolis, IN.
11. Holleman, A.F. and E. Wiberg, 2001. *Inorganic Chemistry*, Academic Press: San Diego.
12. Pre Consultants. Sima. Pro. 7.0, LCA Software: User Manual. Netherlands. <http://www.pre.nl/download/manuals/SimaPro7IntroductionToLCA.pdf>
13. Bare, J.C., G.A. Norris, D.W. Pennington and T. McKone, 2002. TRACI: The tool for the reduction and assessment of chemical and other environmental impacts. *J. Indust. Ecol.*, 6: 49-78.