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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2004/0124093 A1****Jung et al.**(43) **Pub. Date:****Jul. 1, 2004**(54) **CONTINUOUS PRODUCTION AND SEPARATION OF CARBON-BASED MATERIALS****Related U.S. Application Data**

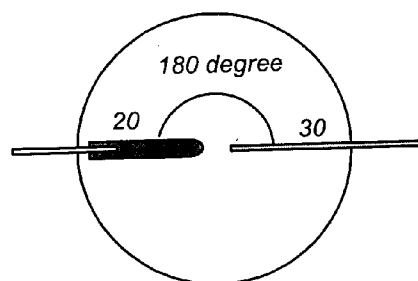
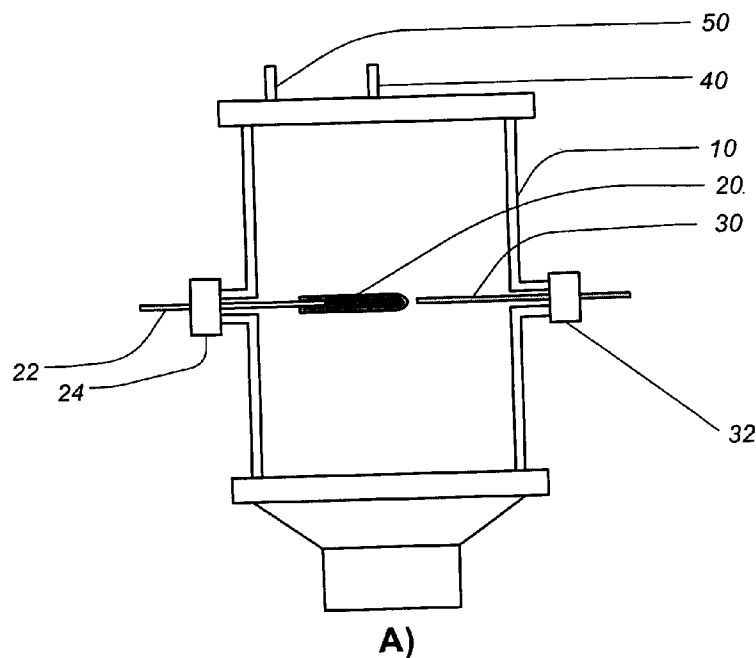
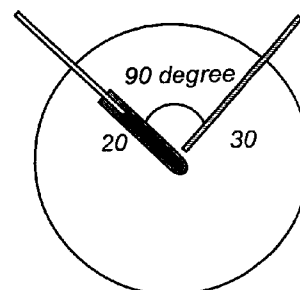
(60) Provisional application No. 60/418,964, filed on Oct. 16, 2002.

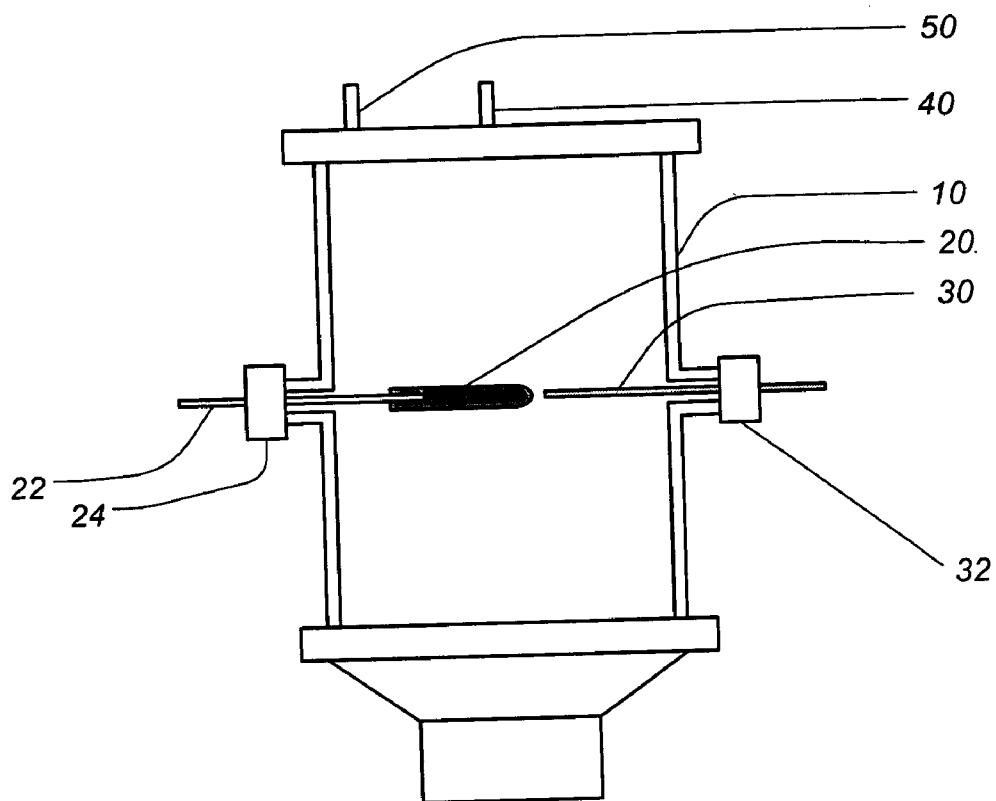
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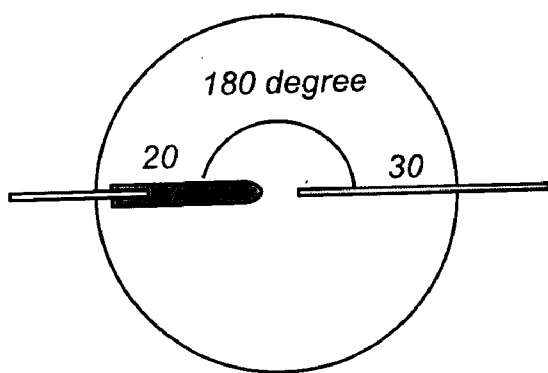
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SALT LAKE CITY, UT 84101 (US)**ABSTRACT**

The invention relates to several apparatuses and methods for the continuous production of carbon soot with a high content of fullerenes, endohedral metallofullerenes (EMFs), and carbon nanotubes. In addition, the invention relates to anaerobic manipulations of carbon-based compounds. The claimed apparatuses and methods provide optimal conditions during annealing processes. In particular, the rotary shielding block of the present invention can effectively prevent resultant products from exposure to intense ultra-violet radiation associated with vaporization processes.

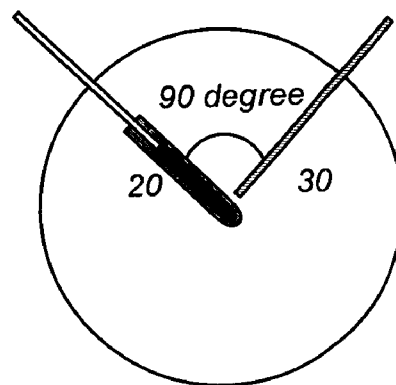
(21) Appl. No.: **10/684,626**(22) Filed: **Oct. 14, 2003****B)****C)**



A)



B)



C)

FIG.1.

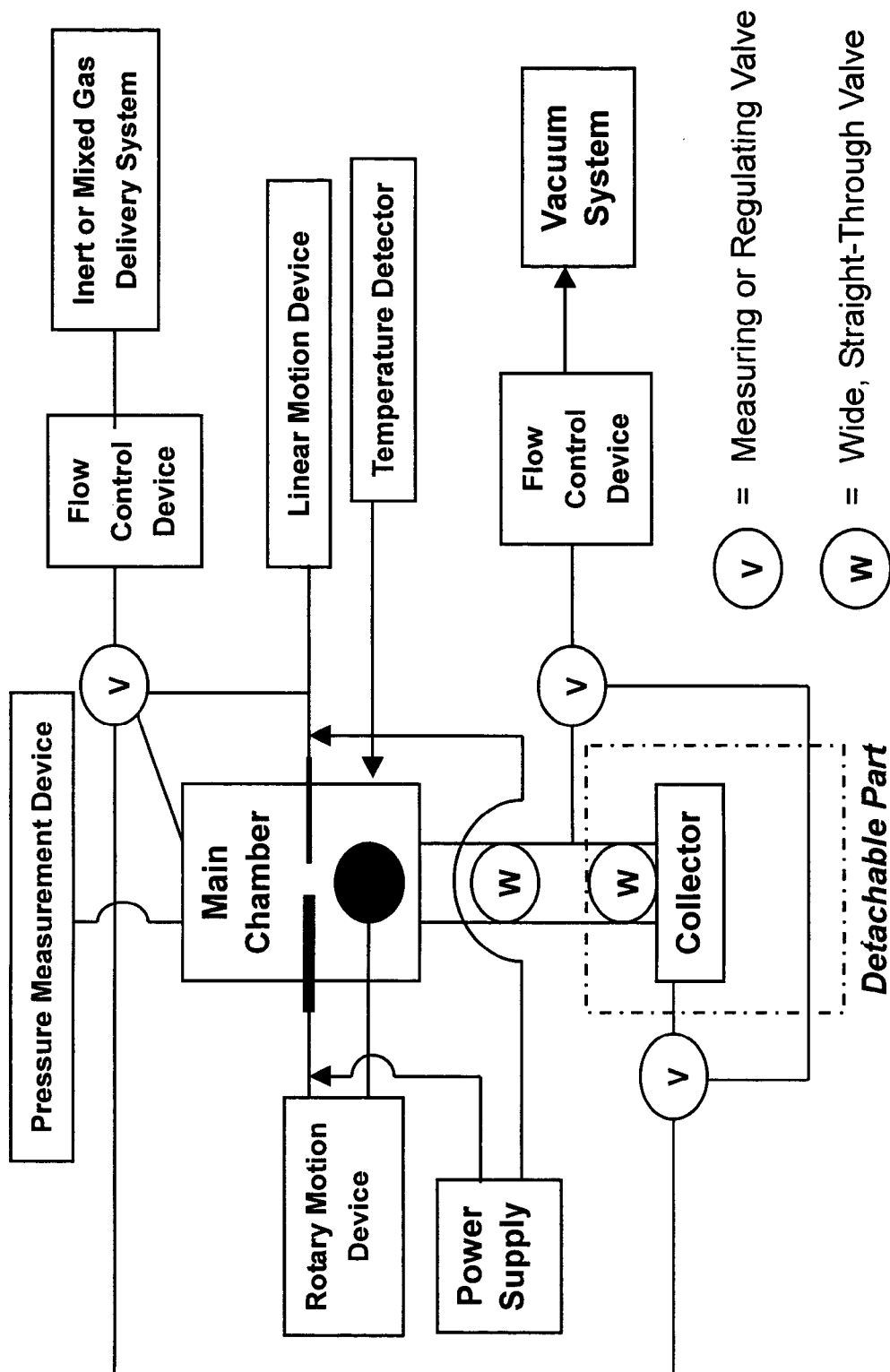


FIG. 2.

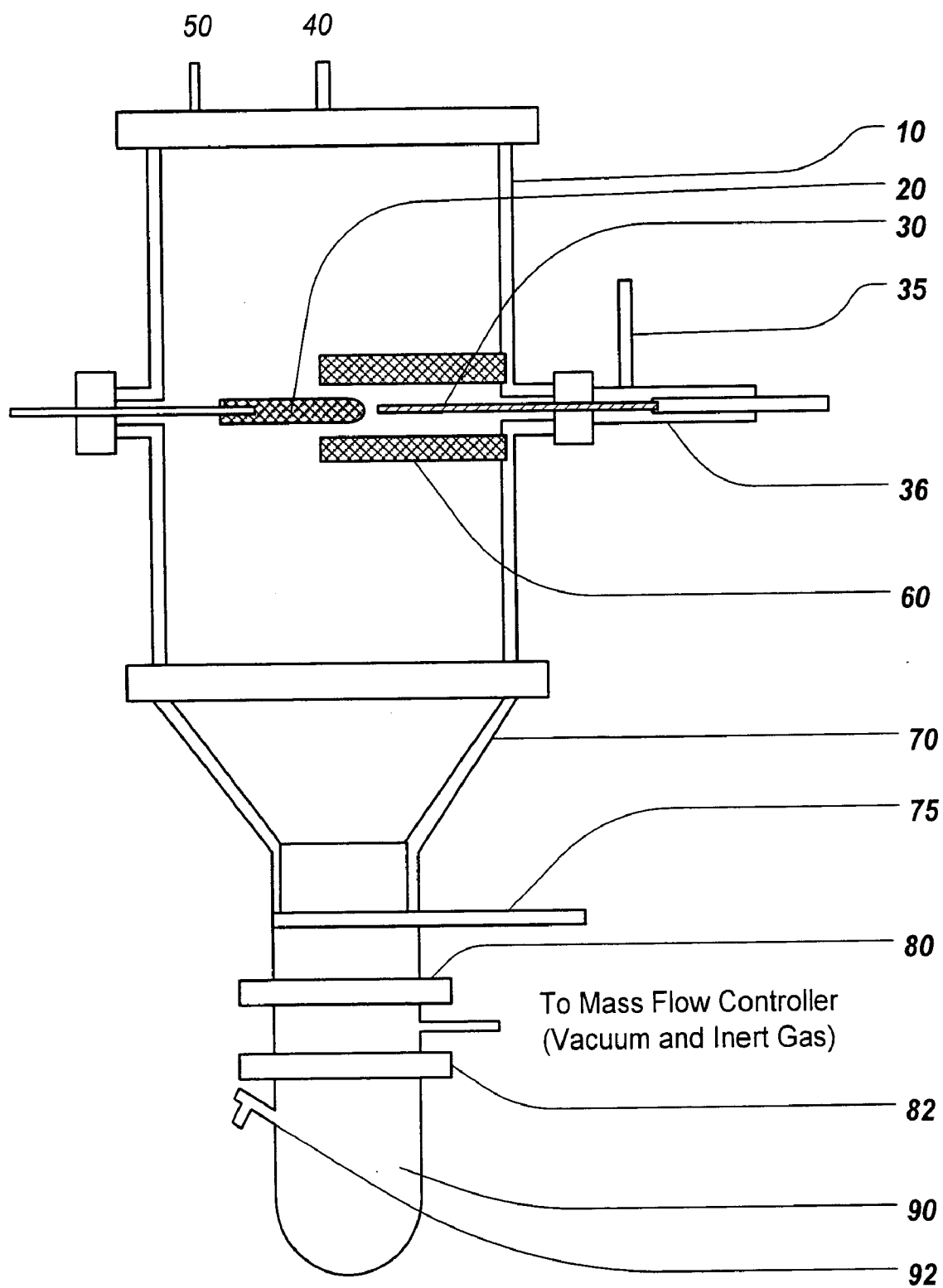
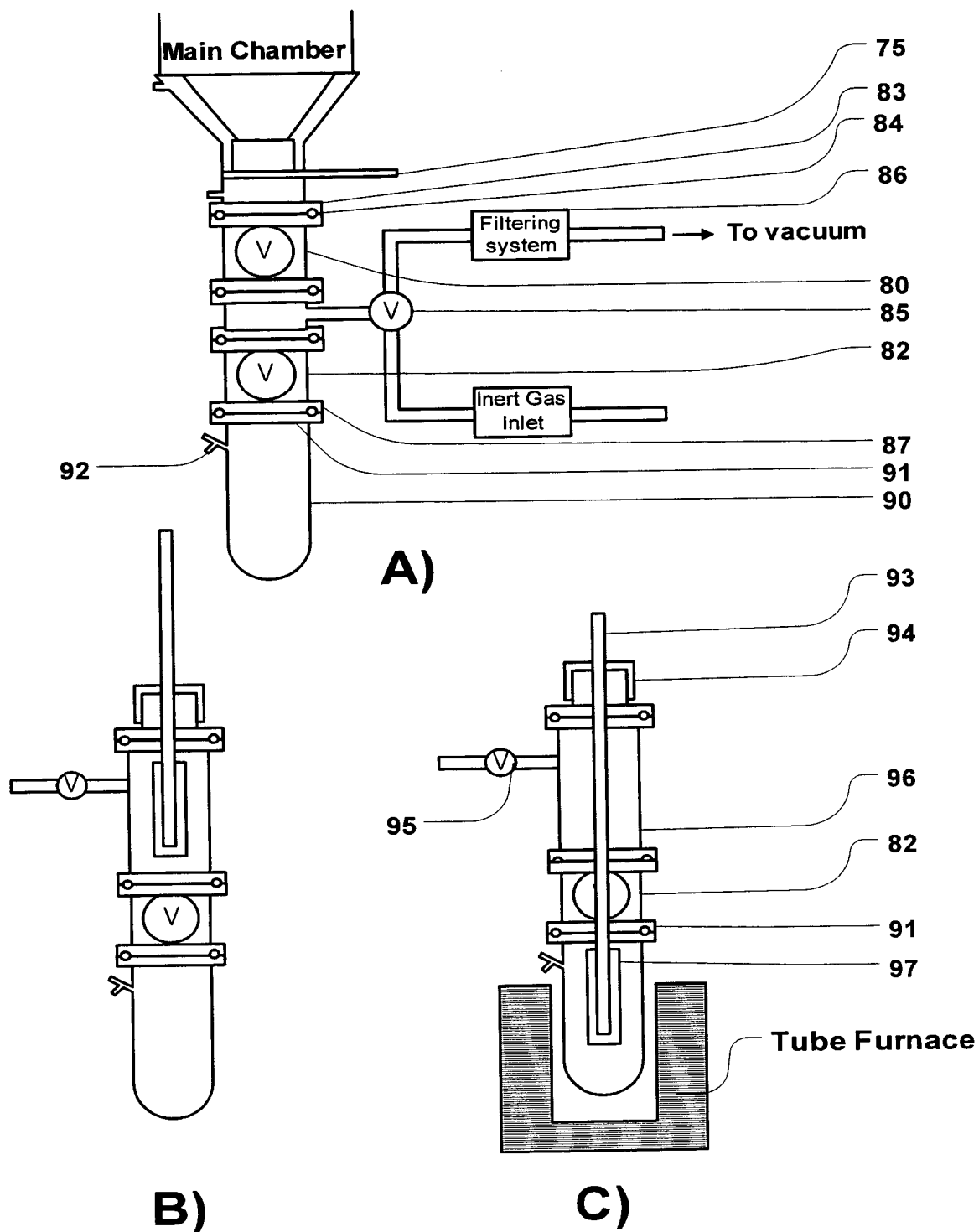


FIG.3.



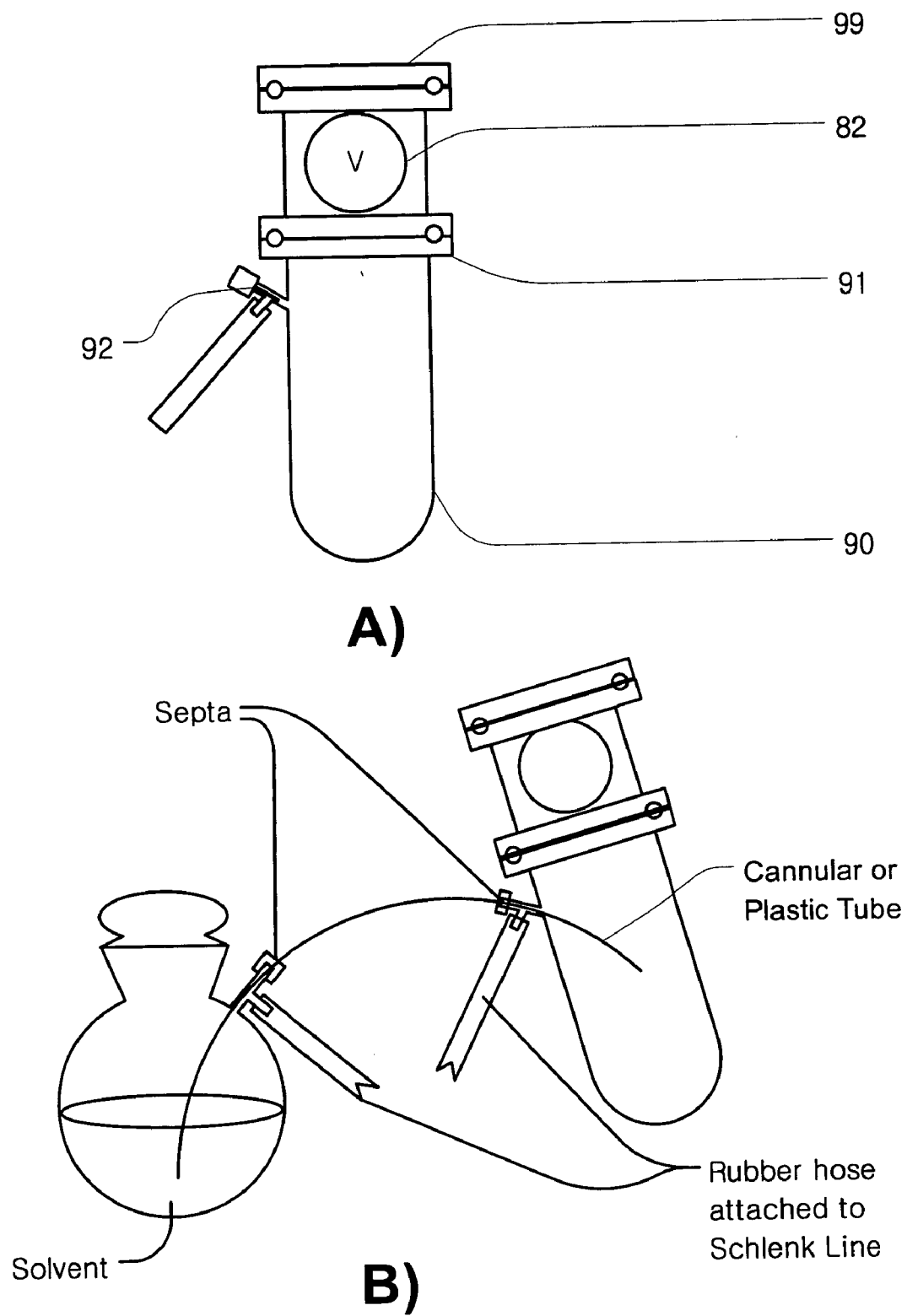


FIG. 5.

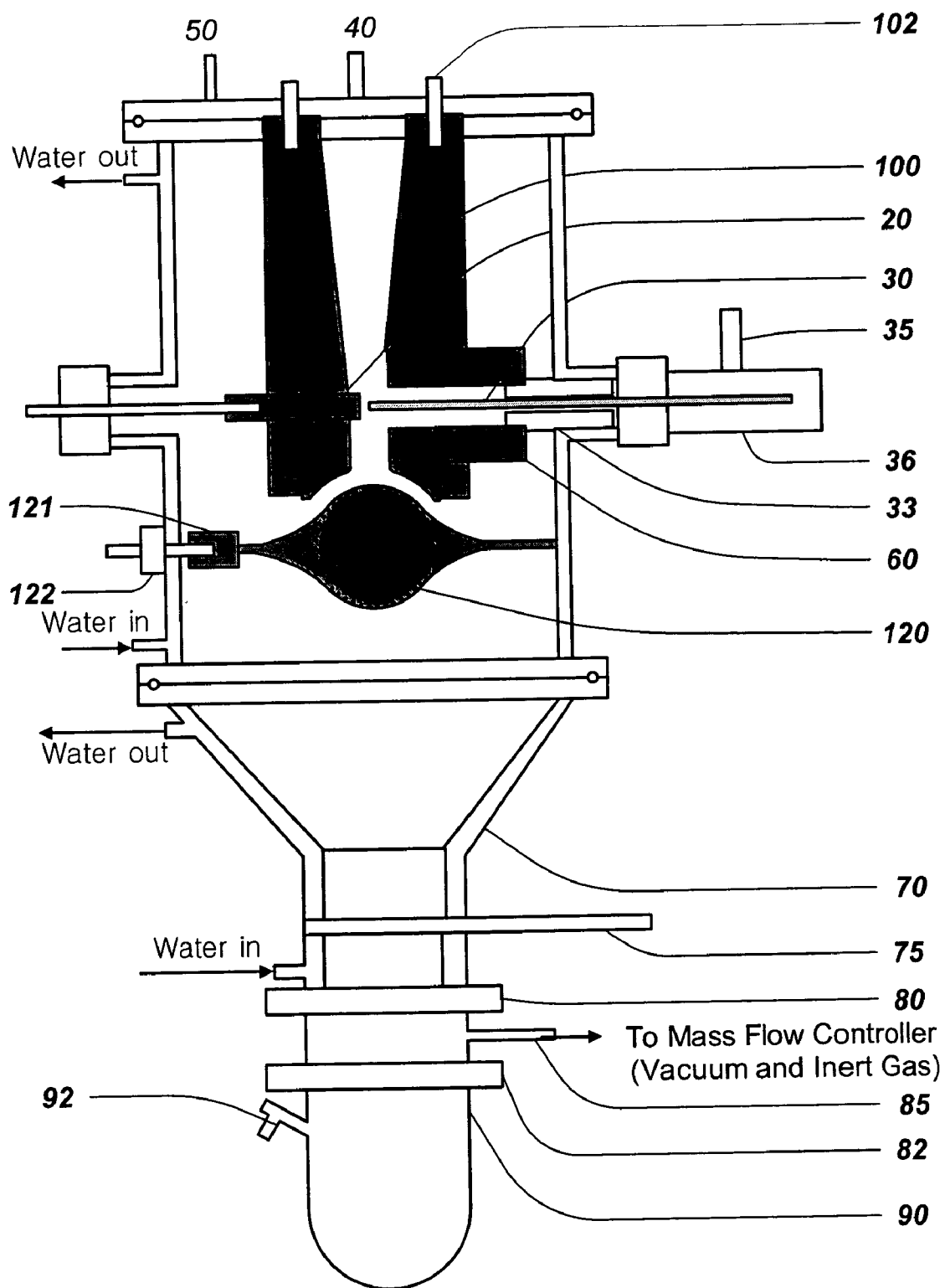
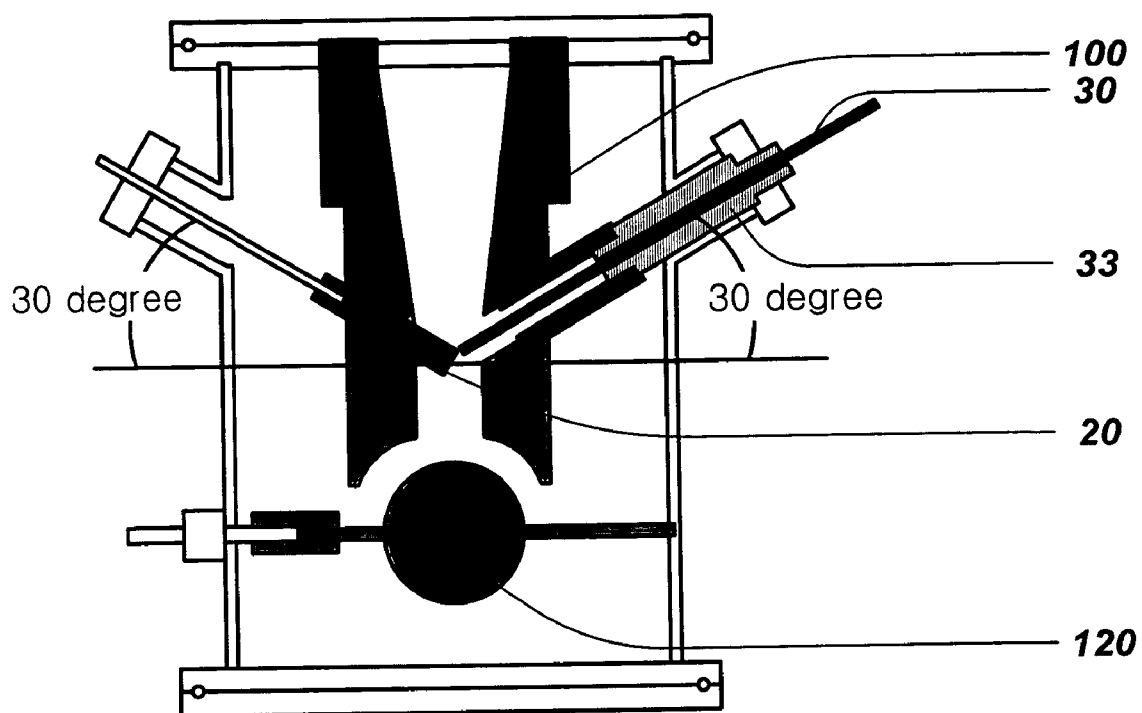
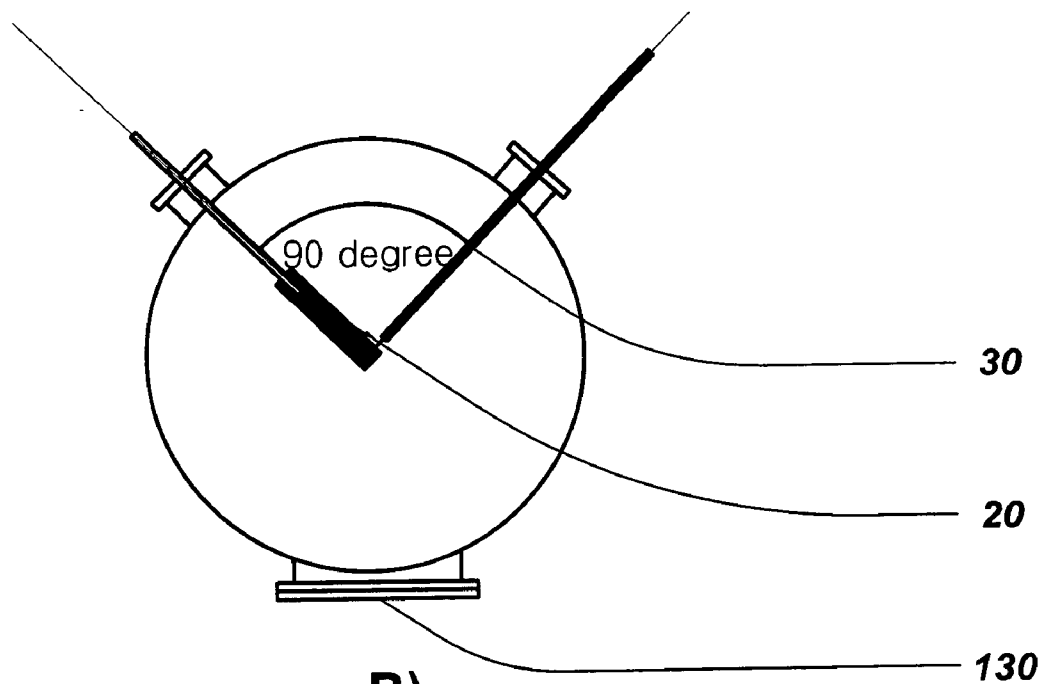


FIG. 6.



A)



B)

FIG. 7.

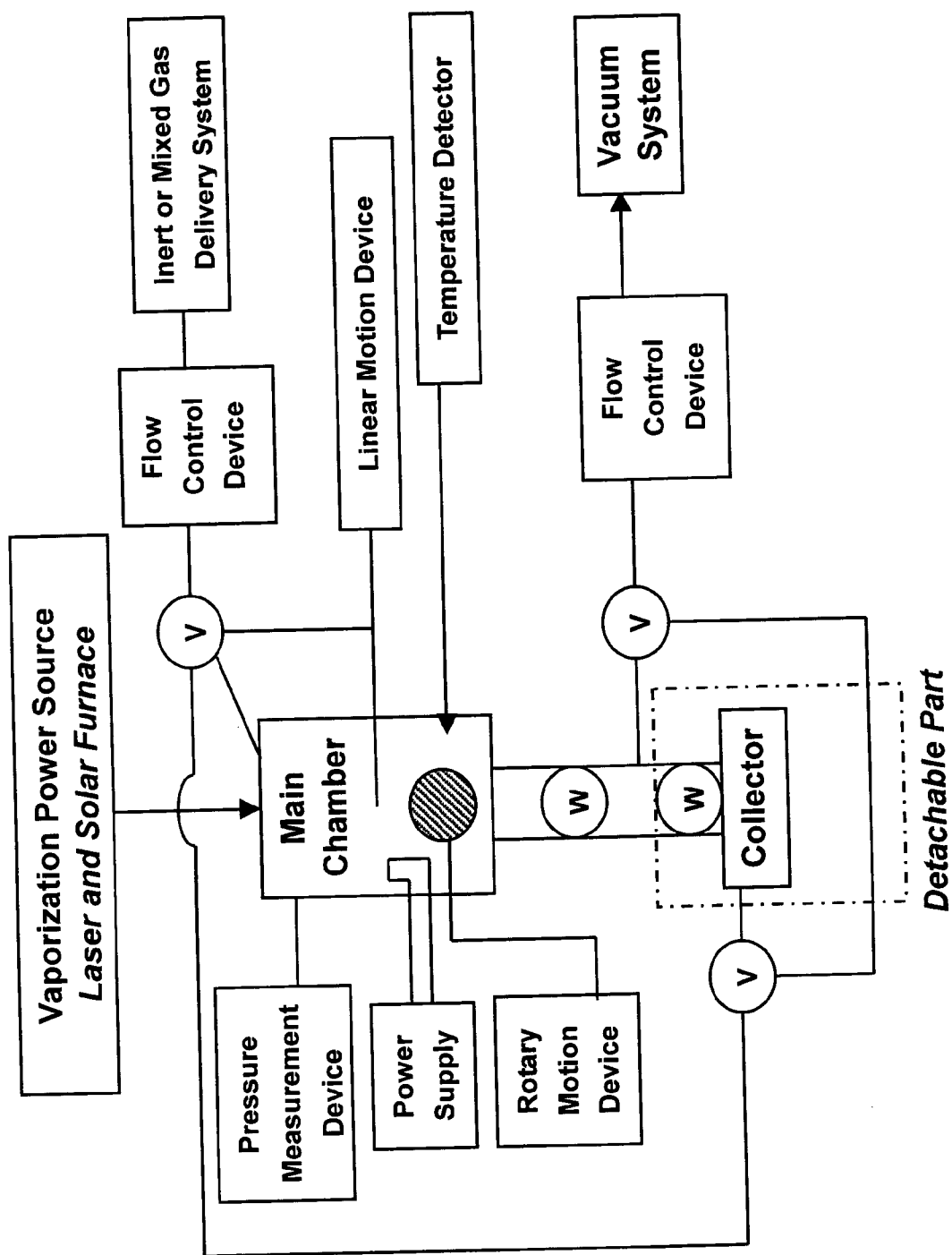
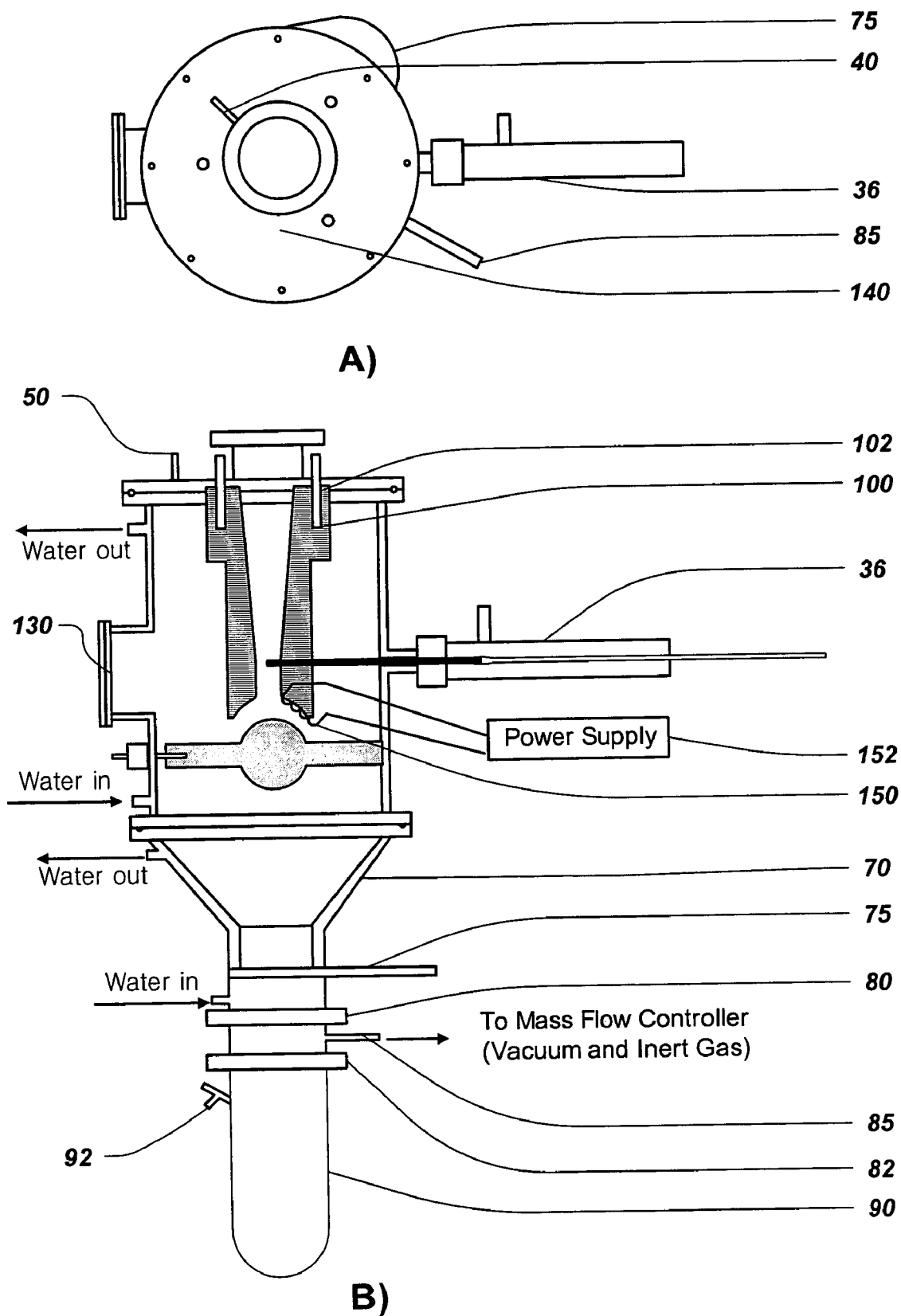


FIG. 8.



CONTINUOUS PRODUCTION AND SEPARATION OF CARBON-BASED MATERIALS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a non-provisional application claiming priority to provisional application Serial No. 60/418,964 filed Oct. 16, 2002.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to an apparatus and a process for optimized annealing during graphite vaporization wherein exposure to intense ultraviolet radiation is minimized. The invention provides mass production methods for fullerenes, endohedral metallofullerenes (EMFs) and other carbon-based materials through effective shielding from destructive UV radiation during graphite vaporization. This provides for slower cooling of the annealed carbon compounds and increased yields of up to 10 times or even better over conventional production techniques.

[0004] 2. Description of the Prior Art

[0005] In 1985, the unique stability of molecular allotropic forms such as C_{60} and C_{70} was demonstrated [H. W. Kroto et al.; *Nature* 318, 162 (1985)]. This event led to the discovery of a whole new set of carbon-based substances known as fullerenes. The configuration of carbon atoms in fullerenes provides unique properties that have captured the interest of chemists, physicists, materials scientists, and medical researchers, as fullerenes have been shown to crystallize to form interesting solids and to polymerize in several ways to form new polymers. Fullerene compounds can be reacted with other chemicals in a number of ways to form new molecules of interest. Tubules of fullerenes, known as carbon nanotubes, have caught increasing interest as fibers, nanowires, and encapsulants. Fullerenes can also be doped to form electronic materials or reacted to form superconductors.

[0006] All of these applications have been discovered since the first macroscopic amounts of the most common two fullerenes, C_{60} and C_{70} , were isolated in 1990 [Krätschmer, et al., *Nature* 347, 354 (1990)]. Much of the work on fullerenes is performed using small amounts of material, as synthetic production of these forms of carbon yielded limited quantities of material. The major drawback to the commercialization of some of the applications mentioned has been the lack of a large-scaled method for producing and isolating fullerenes.

[0007] Synthetic production of fullerenes was first provided using vaporization of graphite in an expanding helium atmosphere [H. W. Kroto, et al., *Nature* 318, 162 (1985)]. In this method, a Q-switched Nd:YAG laser is focused onto a rotating disc of graphite, whereupon carbon is evaporated or ablated into a high-density helium flow. Clusters of soot form and are detected using a time-of-flight mass spectrometer. However, this method of production is sufficient to form only a few micrograms of fullerenes per day, which is only enough for certain, limited research purposes.

[0008] A more useful method of synthesizing fullerene-containing soot is the electric-arc method [Krätschmer, et

al., *Nature* 347, 354 (1990)]. In a variation of this method known as the contact arc process, lightly contacting graphite electrodes are heated electrically by an electric-arc welder in an atmosphere of helium at a pressure of about 50 to about 300 torr. The porous graphite electrodes are vaporized by the arc welder to produce soot containing fullerenes. The soot condenses upon cool walls of a chamber, and is scraped off after the electrodes are consumed. Fullerenes are then extracted from the soot by a solvent, such as toluene, carbon disulfide, toluene, or benzene. This method is capable of producing a few tens of milligrams of fullerenes per run. By running several arc welders in parallel, the process is capable of producing several grams of fullerenes per day. The process is encumbered, however, with scaling problems. For example, as the diameter of the rods gets bigger and the current supplied to the rods gets higher to increase the amount of graphite evaporated per unit of time, the yield of fullerenes decreases. Although the linear decrease in yield with an increase in rod diameter and with a decrease in the angle between the two electrodes is not understood, a reasonable conjecture put forth by Chibante, et al. [(*J. Phys. Chem.* 97(34), 8696 (1993))], is that the intense ultraviolet light in the plasma region of the arc may destroy fullerenes before they can exit that region.

[0009] Howard, et al. in *Nature* 352,139 (1991) discloses a third method of producing fullerenes. This method entails burning hydrocarbon feeds in an oxygen deficient flame or sooty flame. Benzene is used as a hydrocarbon source, with an argon diluted oxygen supply. In this method, it was found that soot yields are 0.2 to 12% of the carbon feed, giving a maximum yield of fullerenes of 0.3% of the carbon feed. This synthesis process has been improved by scientists at TDA Inc., but the process can not be applied to the production of EMFs because metal precursors can not be delivered into the carbon annealing zone.

[0010] Chibante et al, in *J. Phys. Chem.* 97(34), 8696 (1993) and Laplaze, et al, in *Syn. Metals* 86, 2295 (1997) and others, show a fourth method of production using solar radiation. These small scale experiments, using a 2 kW solar furnace, have shown that efficiencies of up to 20% can be reached. However, there is an inherent problem associated with using a solar furnace—the small solar furnace has a weak focus area and larger furnaces require more area to collect solar radiation. Chibante et al, in *J. Phys. Chem.* 97(34), 8696 (1993) studied many other useful experimental parameters on various graphite vaporization techniques, as mentioned earlier. The limitation of the vaporized graphite rod, the angle between the electrode, and temperature dependence of the vaporization have been investigated carefully. As mentioned, shielding of the destructive and intense radiation during vaporization is a novel advance in the production of fullerenes and related carbonaceous compounds.

[0011] The prior art methods of producing fullerenes, namely, laser ablation of graphite targets, the electric-arc process, the solar preparation, and the process whereby soot produced by an oxygen deficient flame is utilized, are encumbered by small production capacities, producing at most only milligram quantities of fullerenes, loss of efficiency as the electrode diameter is increased, and the high expense, low yields of soot from benzene. For these reasons,

current methods of fullerene production are largely impractical. A more economical and scalable method of fullerene production is needed.

SUMMARY OF THE INVENTION

[0012] First, the invention provides an apparatus and method for producing fullerenes, EMFs, carbon nanotubes, and other carbon materials in quantities greater than the few hundred milligrams produced per day by the conventional techniques such as contact-arc, laser ablation, and solar radiation vaporization.

[0013] Second, the invention provides a scalable method for continuously producing fullerenes in greater quantities than the small amounts available through current methods, without losing efficiency in production from increases in the electrode diameters.

[0014] Third, the invention provides an apparatus and method for effectively transferring fullerenes, EMFs, carbon nanotubes, and other carbon materials from the destructive vaporization zone using the constant flow of buffer gas.

[0015] Fourth, the invention provides a method or producing increased amounts of fullerenes, EMFs and other carbonaceous compounds using longer annealing times by using a graphite guide tube, which can be heated by an arc plasma.

[0016] Fifth, the invention provides an apparatus and method for producing increased amounts of fullerenes, EMFs and other carbonaceous compounds under more optimal conditions for delivering metal precursors.

[0017] Sixth, the invention provides an apparatus and method for producing increased amounts of fullerenes, EMFs and other carbonaceous compounds by decreasing the exposure from destructive high energy radiation during vaporization by using a graphite guide tube and a rotary shielding block.

BRIEF DESCRIPTIONS OF THE DRAWINGS

[0018] FIG. 1 shows a prior art apparatus with A) bisectonal view of the conventional contact-arc reactor in prior art, and the different arrangement of the contact-arc electrodes, B) 180 degree angle between the rotary and linear motion graphite electrodes, and C) 90 degree angle between rotary and linear motion graphite electrodes.

[0019] FIG. 2 shows a block diagram of the present invention.

[0020] FIG. 3 shows a bisectonal view of the apparatus with the graphite shielding tube of the present invention.

[0021] FIG. 4 shows A) the detail of the bottom side, B) the connection mode of the separated collector with a sublimator, and C) a sublimation process in a tube furnace.

[0022] FIG. 5 shows A) a Schlenk line collector and B) anaerobic manipulation by using the cannular technique.

[0023] FIG. 6 shows a bisectonal view of the apparatus with a heat reserving guide tube and a rotary graphite shielding block.

[0024] FIG. 7 shows A) a the bisectonal view of the modified apparatus of FIG. 6 of which both electrodes are tilted 30 degrees from horizon and B) the position of two

electrodes, which are perpendicular each other, which are perpendicular each other, from top view.

[0025] FIG. 8 shows another block diagram of the present invention.

[0026] FIG. 9 shows a bisectonal view of the apparatus with laser and solar radiation sources.

DETAILED DESCRIPTION OF THE INVENTION

[0027] Manufacturing fullerenes requires a source of small, gas phase carbon clusters of from 2 to 10 atoms. Two sources of these carbon clusters exist. One is the disproportionation reaction in flame of hydrocarbons or CO in an oxygen deficient flame to produce carbon soot. While the percentage of fullerenes in the soot may seem relatively high, the yield of fullerenes compared to the mass of hydrocarbon consumed is low. The other source is the vaporization of graphite at temperatures above 3000 degree C., whereupon the vaporized carbon is then condensed into carbon soot. While this arc method has proven to be the most useful, even this method yields only tenths of grams of fullerenes per hour. None of the existing methods of production are capable of being adapted for large-scale production.

[0028] The present invention provides an apparatus and a process for optimized annealing during graphite vaporization wherein heat from plasma carbon is directed into a limited area to provide a slower cooling process. The invention uses a shielding block and narrowed gas flow channels to rapidly move vaporized carbon from the area of intense destructive radiation to a shielded condensation area. In addition, the geometric arrangement of the shielding block can further reduce the exposure on products to destructive high-energy UV radiation during vaporization. Under these conditions, yields are dramatically increased and the apparatus can be scaled-up for mass production.

[0029] FIG. 1 shows a conventional electric-arc reactor that is well-known in art. Rotary graphite electrodes (RGE) 20 and linear-feeding porous graphite electrode (LFE) 30 are arranged for arc contact in a stainless steel, water-cooled, double-wall (SWD) chamber 10.

[0030] FIG. 2 shows the block diagram of an electric-arc reactor of the present invention. The collector section can be separated without disturbing the main system and allows continuous collections and anaerobic manipulation of the resultant product soot.

[0031] FIG. 3 shows another embodiment of the present invention. The main chamber 10 is the SWC jacket, which has two O-rings or copper gasket sealed flanges (OSFs or CGFs) attached at both ends or a quartz tube with SWD installed OSF on both ends. After purging the reactor, constant inert gas (typically helium, nitrogen, argon) flow can be set up by a mass flow controller (MFC). Then, electric current is applied to both electrodes (20 and 30), which are electrically insulated, while the constant inert gas flows through inlet valve 35. Carbon clusters from vaporized graphite travel with the inert gas flow. From the Bernoulli Theorem, the flow rate increases when the vaporized soot passes near fixed electrode 20, because of the narrower path. During the vaporization, the guide tube 60 will become heated. Middle chamber 70 is an SWD jacket with a stopper

75 where the vaporized soot is accumulated. During the vaporization process, monitoring of the thermal distribution is accomplished by using a CCD detector or the temperature on the specific part of the reactor through the window **130** (FIGS. 7 and 9), which is not shown in FIG. 3. the change of electric properties, such as conductance, or resistance between two electrodes, can be monitored as well. Final product will be transferred into the quartz collector **90** by opening the stopper **75** and wide-mouth, straight-through, metal or o-ring sealed valves, **80** and **82**. After collecting all the carbon soot from the chamber, the stopper **75** is closed and several inert gas pulses are directed into the chamber to collect soot from the wall. The stopper **75** is then opened to collect the rest of the carbon soot. This process can be repeated several times.

[0032] FIG. 4 shows the bottom part of the apparatus, which can produce carbon-based material in continuous mode. On the collector **90**, an attached stopcock with schlenk connector **92** provides anaerobic manipulation. The Schlenk line is used while valves **80** and **82** are kept closed to keep pressure in the chamber and collector. After valve **82** is closed, the collector **90** can be detached for removal of the carbon materials. An additional flange covers the bottom of the middle chamber **70**, and the valve **85** opens to the vacuum to evacuate all the air from the connection. During collection, an additional sublimator can be attached on top of the valve **82**, and then valve **95** is opened to evacuate all the buffer gas from the sublimator. This cycle of purging and opening is then repeated. The sublimation system can be set up into a tube furnace, and then the valve **82** is opened carefully. The sublimator **97** inserts into the collector, running the cooling water in rod **93**, as a heat exchange system, and then the system is purged until the pressure goes down to 10^{-3} torr by using a secondary diffusion or other high performance vacuum pump. The fraction collected in a certain temperature range gives specific fullerene molecules, as is well known in art. Repeated sublimations provide initial purification of fullerenes and EMFs. Before detaching sublimator with valve **82**, if necessary, additional solvent extraction can be done in anaerobic conditions, as shown in FIG. 5.

[0033] FIG. 5 shows anaerobic manipulations by using Schlenk Techniques. The resultant soot can be transferred to other glassware by using a common Schlenk technique, such as the cannular method. Then solvent extraction can be performed for further separations. In addition, the resultant soot can be transferred without detaching collector **90** by using the Schlenk Technique.

[0034] FIG. 6 shows another embodiment of the present invention. The main chamber **10** will be the SWD jacket or quartz tube, as in FIG. 3. The vaporization area surrounded by a main guide tube (MGT) **100** and a rotary shielding block (RSB) **120** can reserve the heat from plasma and escape the resultant product from the plasma area to minimize exposure high energy UV radiation. The guide graphite tube **100** will be fixed by using a water-cooled feed through valve **102**. Inert gas flow rate through inlet valve **35** can be adjusted by using a MFC. Zirconia tube **33**, or other high temperature resistant material can be used or guide tube **60** can be directly attached on the wall in main chamber **10**. The quartz tube chamber does not need electric insulation, but it needs an additional air-cooling system around the chamber. The cartridge **36** can load several porous graphite rods. After

consuming the feeding electrode, a new porous graphite rod in **36** can be easily replaced without any difficulty. The cartridge **36** can be employed and modified in the bullet loading system from the conventional automatic weapon and others easily available in art. The RSB **120** can be rotated in various speeds with rotary feed-through and an additional scraper directly attached on RSB **120**, if necessary. Rotation of the shield block creates a suction effect, thereby drawing the vaporized carbon particles downstream. Middle chamber **70** is a SWD jacket with a stopper **75** used for accumulating vaporized soot. The collection process is the same as described in connection with the description of FIG. 3.

[0035] FIG. 7 shows another variation of the apparatus of the present invention. As is well-known in the art, product yields vary according to the position of the electrodes. This figure show only one position of the electrodes. In the present invention, the flow of inert gas gives the effective escape of the resultant carbon soot by following the Bernoulli Theorem. Also, the rotation speed of the shielding block **120** is an additional factor in reducing the exposure of the product to UV radiation.

[0036] FIG. 8 shows a block diagram of the apparatus using laser or solar vaporization techniques. The vaporization energy source can be attached to the top of the reactor with the stream of the inert gas flow. In addition, preheating the graphite element can raise the temperature up to 2000 degree C., and gives smoother vaporization and better yields.

[0037] FIG. 9 shows one type of the apparatus of the present invention developed from FIG. 8. Vaporization sources, such as a laser or a solar radiation collector system, is attached on the window **140**. The position of the focal point can be adjusted by using a reflecting system or by changing the lens positions. Before starting vaporization, optional preheating system **152** can be used for smoother vaporization. Heating system **152** is made of a graphite heating element found in commercial vacuum furnaces, which can heat up to 2000 degree C. The heat distributions inside the main chamber can be monitored as mentioned in FIG. 3. The rotation speed of RSB **120** can be affected the efficiency of the production.

[0038] Carbon source materials for producing fullerenes can be selected from among graphite, graphite powder, glassy carbon and amorphous carbon; however, graphite is preferred. A porous graphite rod is also preferred because it has more surface area, including a hemispherical cavity in its top surface. Also, it provides greater amounts of soot containing higher amounts of fullerenes. Moreover, it can be handled very easily. Furthermore, the impregnation of the metal precursor in a porous graphite rod to prepare EMFs is well-known in the art.

[0039] In general, increased yields from the present invention are accomplished by effective shielding and by directing heat from plasma carbon into a limited area of the reactor during vaporization, and by quickly transporting vaporized graphite in flowing inert gas to keep the resultant product

away from the destructive UV radiation area. Fullerene production yields are also affected by the:

- [0040] a) length and diameter of the both end on main guide tube (MGT),
- [0041] b) diameter of the both electrodes,
- [0042] c) number of vaporized electrodes,
- [0043] d) flow rate of inert gas,
- [0044] e) mixed ratio of inert gas,
- [0045] f) interval of the vaporization process,
- [0046] g) rotation speed of the shielding block (in FIGS. 6 and 9),
- [0047] h) geometry of the electrodes and number of electrodes (FIG. 6),
- [0048] i) mixed ratio of inert gas, if necessary, (He, N₂, Ar, and others)
- [0049] j) preheating temperature for inert gas, and
- [0050] k) energy source on vaporization.

[0051] In the present invention, EMFs can be produced by the vaporization of metal compound impregnated porous graphite rods and other metal containing carbon sources. Various metal impregnation processes on porous graphite rod are readily available from the prior art. For example, the soaking method [Cagle et al, JACS, 118, 8043 (1996)] has been developed, and the content of the metal precursor on the graphite rod can be controlled by the concentration of the metal compound solution. Metal impregnated graphite rods can be purchased from Toyo Tanso, Co, in Japan. [Shinohara, et al, Bioconjugate Chem., 12, 510 (2001)]

[0052] Table 1 shows some EMFs obtained from the present invention. The previous reported trimetallic nitride template (TNT) process [Dom, et al, Nature, 401, 6748 (1999); U.S. Pat. No. 6,303,760 (2001)] can also be easily adapted. Various metal compositions on graphite rod can be controlled and can be easily investigated to reach optimal conditions of EMF production. The present invention will expand the currently available EMF family to all transition metals and other metal elements, because of the optimal conditions for metal precursor delivery. Placing boron and nitrogen atoms into the cage structure is possible using boron doped graphite rod, and using partial pressure of nitrogen as a buffer gas.

[0053] In prior art on EMF production, only minor variations on Krättschmer-Huffmann generator [Krättschmer, et al., Nature 347, 354 (1990)] have been investigated. The present invention offers a major overhaul in the production of EMFs and higher fullerenes over 80 atoms in cage.

[0054] Table 1 the possible combination of EMFs between endohedral portion and fullerene cages

Endohedrals	Cage	Remark
M _a	C _{2n}	a = 1-3, b = 0-2
M _a L _b K _{a-b-3}		C = 1-2

-continued

Endohedrals	Cage	Remark
M _a N _c		d = 1 or higher, n = 30 or higher
M _a L _b K _{a-b-3} N _c		M, L, K = metal; N = nitrogen

[0055] The foregoing description is illustrative only of the principals of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described. Accordingly, all suitable modifications and equivalence may be resorted to within the scope of the invention.

What is claimed is:

1. Apparatus for manufacturing carbon compounds, comprising:

a first electrode proximate a second electrode and defining a gap thereinbetween for producing carbon compounds;

a first chamber extending around said gap and defining a first effective cross-section and a second effective cross-section, said second effective cross-section being downstream of said first effective cross-section and having a size less than said first effective cross-section;

a second chamber in fluid communication with said first chamber;

a gas inlet in fluid communication with said first chamber; and

a gas entering through said gas inlet, flowing through said first chamber and across said gap, said gas carrying the carbon compounds into said second chamber.

2. The apparatus of claim 1 wherein said first electrode comprises a linear-feeding porous graphite electrode and said second electrode comprises a rotary graphite electrode.

3. The apparatus of claim 2 wherein said first electrode has a smaller cross-sectional area than said second electrode.

4. The apparatus of claim 1 further comprising a soot accumulation chamber in fluid communication with said second chamber.

5. The apparatus of claim 4 further comprising a collector apparatus connected to said soot accumulation chamber.

6. The apparatus of claim 5 wherein said collector apparatus continuously collects the carbon compounds.

7. Apparatus for manufacturing carbon compounds, comprising:

a first electrode proximate a second electrode and defining a gap thereinbetween for producing carbon compounds;

a first chamber extending around said gap and defining a first effective cross-section and a second effective cross-section, said second effective cross-section being downstream of said first effective cross-section and having a size less than said first effective cross-section;

a second chamber in fluid communication with said first chamber;

a gas inlet in fluid communication with said first chamber;

a shield; and

a gas entering through said gas inlet, flowing through said first chamber and across said gap, said gas carrying the carbon compounds past said shield into said second chamber.

8. The apparatus of claim 7 wherein said first electrode comprises a linear-feeding porous graphite electrode and said second electrode comprises a rotary graphite electrode.

9. The apparatus of claim 8 wherein said first electrode has a smaller cross-sectional area than said second electrode.

10. The apparatus of claim 7 further comprising a soot accumulation chamber in fluid communication with said second chamber.

11. The apparatus of claim 10 further comprising a collector apparatus connected to said soot accumulation chamber.

12. The apparatus of claim 11 wherein said collector apparatus continuously collects the carbon compounds.

13. The apparatus of claim 7 wherein said shield defines said first chamber.

14. The apparatus of claim 7 wherein said shield rotates.

15. The apparatus of claim 14 further comprising means for scraping accumulated carbon compounds from said shield.

16. Apparatus for manufacturing carbon compounds, comprising:

a first chamber in fluid communication with a second chamber;

a vaporization location within said first chamber;

means for producing carbon plasma at said vaporization location;

means for directing a carrier gas from said first chamber into said second chamber;

means for increasing gas flow across said vaporization location;

means for shielding said vaporization location from said second chamber.

17. The apparatus of claim 16 wherein said means for producing carbon plasma comprises opposing first and second graphite electrodes defining a gap thereinbetween for producing carbon compounds.

18. The apparatus of claim 16 wherein said means for increasing gas flow comprises a shield having a first effective cross-section and a second effective cross-section, said second effective cross-section being downstream of said first effective cross-section and having a size less than said first effective cross-section;

19. The apparatus of claim 16 wherein said means for shielding defines said first chamber.

20. The apparatus of claim 16 wherein said means for shielding comprises a rotating spheroid.

21. The apparatus of claim 16 wherein said apparatus is continuously operated.

* * * * *