“Be a Scientist, Save the World”

-Dr. Richard Smalley

Design of a 3-phase AC Plasma Reactor for Solvent-free Fullerene Synthesis

by

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Abstract

Fullerenes are spherical carbon molecules with unique chemical and physical properties. A particularly distinctive one is that these molecules have a vapor pressure and can directly sublime from a solid phase to vapor. Since their discovery in 1985, hundreds of articles have been published on numerous synthesis methods. However, a process which is environmentally friendly, continuous, scalable and efficient has yet to be achieved. We propose a system for continuous production of solvent-free manufacture of fullerenes using a novel 3-phase thermal plasma reactor. It is scalable, self-stabilizing, low maintenance and efficient. Helium is used as plasma carrier gas with temperatures >5000°C allowing for vaporization of any carbon feedstock. Fullerene yields of up to ~7 wt% at 1 bar absolute were measured, a higher yield than any other known process. Once the fullerenes are produced, they are then separated using a hot gas sublimation at >600°C which allows for solvent-free separation of fullerenes, resulting in an ultrapure product.

Economic analysis of a small pilot reactor indicated a net annual profit of 0.75 million CAD at the pilot scale with a capital investment of 2 million CAD. The cost of sublimed fullerene per gram is estimated to be about ~ 7.8 CAD/g which is substantially lower than its current selling price of 24-102 CAD/g. These results validate the efficiency, scalability, economic feasibility and viability of the process. Hence, the route to environmentally friendly production of solvent-free fullerenes on a commercial scale at affordable prices is soon realizable.

Dedication

To Mom and Dad.

Acknowledgment

I would like to start by thanking the UNB machine shop for providing us with quality parts quickly. I would like to thank Dr. Chibante for his mentorship and freedom allowing me to explore research avenues no matter what the cost provided I supported it with sound scientific reasoning. I would like to thank all the members of the Applied Nanotechnology Laboratory for teaching me various skills and trusting me with some unconventional experimentation throughout the years.

Friends played a vital part in this journey from listening to me and being there through both good and bad days to helping me de-stress. It has been quite a journey, and a lot of people have stood by me and supported me; I would like to thank you all for being amazing people.

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Nomenclature

Abbreviations and Symbols	
abs	Absolute
AC	Alternating Current
ANL@UNB	Applied Nanotechnology Laboratory at University of New Brunswick
DC	Direct Current
EBITA	Earnings before interest, taxes, and amortization
EBT	Earnings before taxes
FDA	Food and Drug Administration
HPLC	High-Performance Liquid Chromatography
IR	Infra-red
INC	Incorporated
k	Kilo
LII	Laser-Induced Incandescence
m	Milli
MHD	Magnetohydrodynamics
MOC	Material of Construction
NPT	Nominal Pipe Thread
µ	Micro
n	Nano
PAH	Polyaromatic hydrocarbons
PCBM	Phenyl-C61-butyric acid methyl ester
RF	Radiofrequency
SS	Stainless steel
TEM	Transmission Electron Microscope
TGA	Thermo-gravimetric Analysis
UV-Vis	Ultraviolet-visible

Units	
A	Ampere
bara	Bar absolute
°C	Degrees Celsius
CAD	Canadian Dollar
G	gram
gpm	Gallons per minute
H	Henry
hr	Hour
Hz	Hertz
K	Kelvin
L	Liter
lpm	Liters per minute
m	Meter
m^3	Cubic meter
min	Minute
Pa	Pascal
psi	Pounds per square inch
rpm	Revolutions per minute
s	Second
USD	American Dollar
V	Volts
W	Watt
yr	Year

1 Introduction

1.1 Overview

Fullerenes are the third form of pure carbon after diamond and graphite; they are perfect spheres about 1 nanometer in diameter. Carbon has four valence electrons and a ground state configuration of $2s^2 2p^2$, and it can bond in different ways to form unique materials with different properties.

Graphite is a soft grey solid which is composed of sheets of trigonally bonded carbon atoms arranged in hexagonal sheets called graphene sheets (as shown in Figure 1: Atomic structure of graphite) and has a high electrical conductivity along the direction of the sheets. Diamond is a hard solid which is an electrical insulator which is composed of tetrahedrally bonded carbon atoms (Figure 2: Atomic structure of diamond) formed under extreme pressure and temperature.

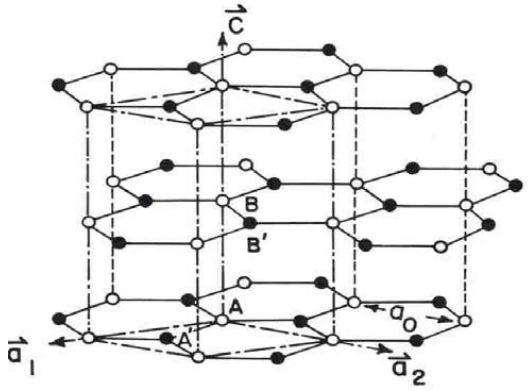

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Figure 1: Atomic structure of graphite

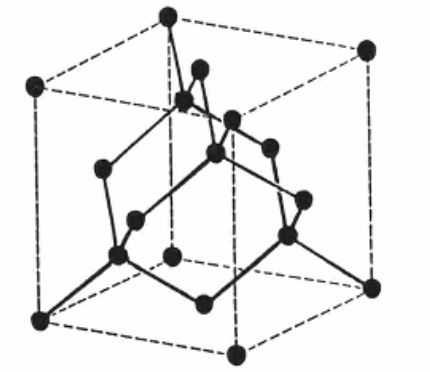

Figure 2: Atomic structure of diamond

Carbon atoms exhibit sp^2 hybridization in graphite, each atom is evenly connected to three carbon atoms in the x-y plane, and a weak π bond due to the p_z orbital is present in the z-axis. In diamond sp^3 hybridization occurs where four bonds are directed towards the corners of a regular tetrahedron to form an extremely rigid three-dimensional structure which is responsible for the hardness [1].

The free electrons in the p_z orbital of the graphite lattice are delocalized and free to move within the framework whereas all the electrons in a diamond are localized. This is responsible for the conductivity of graphite and the diamond behaving like an insulator, respectively

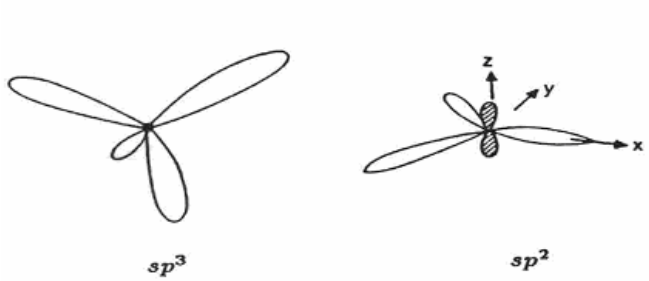

Figure 3: Hybridization of diamond (sp^3) and graphite (sp^2)

In 1985 Harold Kroto, Richard Smalley, and Robert Curl were researching the synthesis of polyynes by laser vaporization of a graphite target when they discovered unusually stable peaks of carbon clusters in the mass spectrometer. After much research they determined the first stable cluster to be a closed cage molecule which resembled the geodesic domes designed by R. Buckminster Fuller and thus named them fullerenes. The most famous fullerene is the C_{60} molecule also referred to as the buckminsterfullerene or buckyball as shown in Figure 4: Fullerene C60 structure.

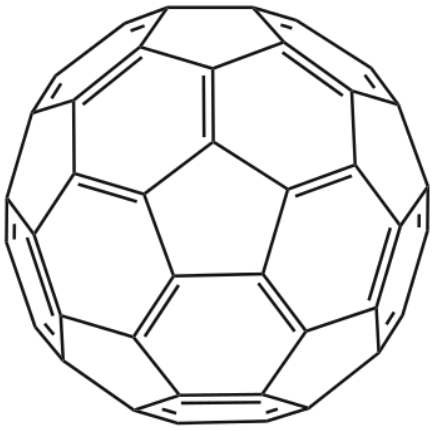

Figure 4: Fullerene C_{60} structure

Several synthesis methods exist today, including the carbon arc method, solar synthesis, combustion synthesis, and plasma synthesis. In all these methods, carbon vapor is made to condense into spherical cages at high temperatures.

The product (soot) from these synthesis methods typically contains a mixture of fullerenes, amorphous carbon and polyaromatic hydrocarbons (PAH). However, the ratio of these constituents varies from process to process depending on the reaction conditions. Consequently, various purification techniques have been developed to separate fullerenes from the impurities.

The synthesis and post-synthesis techniques for fullerenes are discussed further in chapter two and appendix A.

1.2 Structure & properties

The discovery of fullerene by Smalley and coworkers in 1985 pioneered a new direction in carbon research. C_{60} molecule consists of 60 carbon atoms arranged as 12 pentagons and 20 hexagons. C_{60} resembles an American soccer ball(Figure 5: Fullerene soccer ball schematic) where each vertex represents a carbon atom. The proposed structure for C_{60} is that of a truncated icosahedron which is achieved by snipping off each of the twelve vertices of an icosahedron (polyhedron with 20 faces), thereby replacing each vertex by a pentagon. It also converts the twenty triangular faces to hexagons.

Figure 5: Fullerene soccer ball schematic

Smalley and coworkers deemed fullerene to be the roundest molecule that could possibly exist. Each carbon atom connects two hexagons and a pentagon; it has two single bonds and a double bond for its valency of 4. This would lead us to believe its sp^2 hybridized just like graphite with two sigma and one π bond. The p_z orbital in graphite all lie parallel to each other in one plane, but the fullerene molecule is spherical. This adds a strain on the bonds, but because the molecule is spherical, the strain is equally dispersed allowing the spherical structure. This complexity has resulted in varying theories by scientists concerning hybridization the most recent being $sp^{2.3}$ hybridization [2]. Euler's theorem shows that a spherical surface entirely built up from pentagons and hexagons must have exactly 12 isolated pentagons. Depending on the number of hexagons, molecules of different sizes can be obtained. [3]

$$\text{Hexagons} = \frac{(\text{Carbon Atoms}) - 20}{2}$$

Equation 1: Euler's theorem

1.3 Applications

Fullerenes have unique chemical and electrical properties along with a cage-like structure that provides diverse research for numerous applications by scientists across the globe. Their applications include nano-diamond synthesis [4], cosmetics [5], optics [6], solar cells [7], drug delivery agent [8] for cancer treatment as well as nanolithography [9] and lubricants [10] to name a few. Such a wide array of applications assures the continued broad growth of the fullerene market.

1.3.1 Biological

C_{60} is a potent scavenger of free radicals which is why many expensive anti-aging facial creams use it in concentrations of up to 9% by weight [11]. C_{60} in olive oil is the new health supplement after a study by Baati et al. was released in 2012. The study fed C_{60} / olive oil to a controlled group of Wistar rats, and it increased their life span by almost double [12]. It is not FDA approved as the tests with fullerenes, and its additives are still *in vitro*. Researchers have determined oxidative stress plays a vital role in many pathological conditions such as cancers, neurodegenerative disorders (Parkinson's, Alzheimer's and multiple sclerosis), diabetes mellitus, rheumatoid arthritis, atherosclerosis, and hypertension as well as physiological processes like aging [13] [14] [15] [16] and the antioxidant and free radical scavenging properties of fullerenes can help reduce these. Fullerene endohedrals like Gd-based metallofullerenes are used as MRI contrast agents due to their high relaxivity and paramagnetic properties.

The cage structure, small size, and reactivity, which allows for other functional groups to be attached to its cage, make fullerenes ideal for targeted drug delivery in cancer

[17] [16] and osteoporosis [16] [18]. Fullerene has also been used as a neuroprotective agent in the form of carboxyfullerenes to use its antioxidant properties in biological systems [19] [16]

1.3.2 Solar cells

Silicon solar cells have been around for quite some time now and have been optimized for an impressive maximum efficiency of 30%. The manufacturing costs are being reduced, and solar cells are relatively cheap to purchase. However, the installation and maintenance of these cells are where the real cost to customer lies. Not to mention the greenhouse gases emitted while producing silicon. Silicon solar cells require valuable real-estate for installation such as rooftops or straight up land which can be hard to come by in today's concrete cities.

Fullerene derivative [6,6]-phenyl-c61-butyric acid methyl ester (PCBM) is used in organic solar cells as electron acceptors. Typically, these organic solar cells achieve an efficiency of about 5% which is substantially lower than silicon; however, they are extremely light and easy to install. They can be used along the side of buildings and can also replace windows as they can be made semitransparent. Other applications for thin plastic solar cells could also include camping, or as a part of an emergency car kit, the uses are endless because traditional solar cells are bulky and not portable thereby limiting their usage to large scale power generation. [20] [21]

1.3.3 Lubricant

Machines have moving parts and when parts move they experience friction. This friction is responsible for increased energy consumption to overcome friction and the costs to manufacture wear related spare and replacement parts and cost of maintenance work. Friction costs industry a universal average of 18,000 euro for every terajoule of energy consumed [22]. Lubricants are used to reduce friction thereby reducing wear and increasing the life span of the machinery. The newest addition to the lubricant family is nano-enhanced lubricants which are essentially fullerenes mixed with synthetic oil [23]. Multiple products providing nano-enhanced engine treatment such as Nglide [24], XTC 60 [25] are others on the market.

2 Statement of the problem

Current fullerene production on the industrial scale is primarily done using the combustion method, which involves the incomplete combustion of carcinogenic organic solvents like benzene/toluene to produce carbon soot containing fullerenes [26] [27] [28]. The process has various drawbacks, to name a few it uses large amounts of carcinogenic organic solvents as fuel for combustion to produce CO/CO_2 and polyaromatic hydrocarbons (PAH) [29] [30] [31]. The best soot formation efficiency is a meager 10% (generally operated at about 5%), which entails the remaining 90% of the carbon is emitted in the form of greenhouse gasses. The 10% soot collected optimistically contains 10-12% extractable fullerenes thereby making the overall efficiency for fullerene production 1% [32]. Once this soot is produced the fullerenes are then extracted using organic solvents like 1,2,4- trimethylbenzene followed by chromatography column separation. Ultra-pure fullerenes are then obtained by subliming these solvent separated fullerenes and then cooling the vapor, Applied Nanotechnology Laboratory (ANL) has detected trace quantities of these carcinogenic solvents even after sublimation in these products. Since fullerenes are used in the medicinal and cosmetic industry amongst others, the presence of these carcinogens even in trace quantities raises significant concerns with respect to the potency and safety of the product.

The research question that comes to mind is that can solvent-free fullerenes be produced using a cheap and efficient process with a low carbon footprint to aid market growth? The solution is the design of a 3 phase AC high-temperature plasma reactor and a solvent-free extraction system. Reactor design requires an understanding of many variables

such as power, pressure, plasma gas flow rate, and purity, carbon flow rate and purity. Their effect on the plasma stability and the yield of fullerenes in the carbon soot is essential to the design of an efficient plasma reactor.

The research problem is the design of a solvent-free fullerene production process with a low carbon footprint and high conversion resulting in a low-cost sublimed fullerene mixture to aid market growth.

3 Objective

The objective of this project is to design a solvent-free, high purity fullerene production process with a low carbon footprint and high yields of ≥5% thereby resulting in cost reduction of sublimed fullerene mixture to <10 CAD/g in comparison to the current market price of 24-102 CAD/g thus making fullerene-based products readily available. The reactor will be constructed on a pilot scale, and preliminary tests will be conducted. A proof of concept solvent-free extraction system will also be designed and tested, and a small-scale economic analysis was done to validate the objective.

4 Significance of the study

The new process is expected to give improved yields compared to the currently available methods, which have an extremely high carbon footprint at a higher production cost. The current price of fullerene mixture is 24-102 CAD/gram [33] and has plateaued in the last decade because of the low yield and high feedstock/processing costs in the combustion process. The combustion process emits large quantities of greenhouse gases. It uses about 1700 barrels of solvent for every ton of fullerene extracted not to mention the

tons of solvent-laden soot left after extraction needing disposal. These costs have affected the availability of commercial products using fullerenes. By the end of this study, a price drop below 10 CAD/gram should be feasible.

A novel approach is taken in this study for production of fullerene in large quantities at a reasonable cost, based on a new 3-phase plasma reactor design with the capability of operating at sub-atmospheric conditions and minimized electrode erosion. The proposed design shall have stable plasma and will have minimal effects by electrode ablation.

This goal will be accomplished by using existing knowledge to design a reactor with improved yield and reduces operational costs all while decreasing carbon footprint. The innovative approach to recover fullerenes without solvents allows the depleted soot to be recycled back into the feedstock stream while keeping the sublimed product solvent free. Conceivably, this process could result in a 100% conversion of input carbon exiting the closed system as pure fullerene powder without using a drop of organic solvent. These improvements should result in a ten-fold reduction in production costs, all while improving the quality of the product and decreasing the carbon footprint.

The Applied Nanotechnology Laboratory (ANL) has designed its first reactor and has already proven evaporation of carbon to vapor using the system. Trace quantities of fullerenes have also been detected although no feasible quantity has been collected for meaningful quantitative measurements. The goal of this study is to improve the existing design (Mark I) and make the required changes the reactor to achieve the goal.

5 Literature review

The structure, properties, and applications of fullerenes were presented in the last chapter. In this chapter, the synthesis, growth processes and extraction of fullerenes will be reviewed. The literature review of various laboratory scale processes and the influence of design parameters on the yield will be discussed.

5.1 Fullerene synthesis

Fullerenes can be synthesized using different techniques, namely combustion synthesis, and plasma synthesis. Other technologies include electric arc discharge, laser ablation, solar synthesis, etc. Presently, active research is being aggressively pursued on these methods, and different alternative strategies are being developed to find more economical ways of producing these unique and novel materials.

In the combustion synthesis method, fullerenes are produced by the incomplete combustion of organic solvents under fuel rich conditions. The plasma synthesis technique involves the evaporation of a graphite powder by a high–power thermal plasma, under an inert atmosphere at sub-atmospheric conditions.

In this section, the production techniques mentioned earlier will be described, while a detailed review of the literature of fullerene processes, growth mechanisms, and post-synthesis purification methods will be discussed later in this chapter and appendix A.

5.1.1 Electric arc discharge

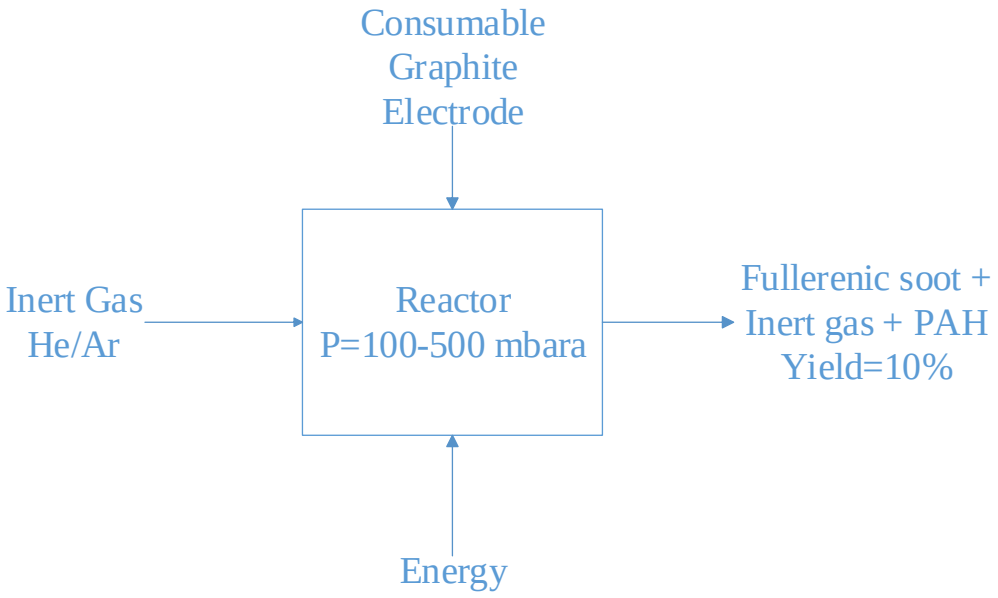

Figure 6: Electric arc discharge block flow diagram

Fullerene production using electric arc discharge is one of the easiest methods to produce fullerenes. It consists of either an AC or DC power source, two graphite electrodes, and a sealed chamber. It also requires an inert gas such as argon or helium and a vacuum pump. The electrodes are connected to the power source and are placed inside the sealed chamber; the vacuum pump is used to purge out all the air followed by injecting some inert gas. Typical pressures are maintained between 100-500 mbar absolute, once the chamber is ready the power supply is turned on, and the arc is initiated by bringing the electrodes closer together or by touch if necessary. Once the arc is generated the electrodes start to evaporate and erode; this serves as the carbon feedstock for fullerene production. The electrode gap is maintained by feeding the graphite electrodes. Once they are consumed

the run is stopped, and the soot is scraped off from the chamber. Fullerene yields in the soot are about 10% with a maximum fullerene production rate of about 10 g/hr. A typical setup for an arc discharge reactor is shown in Figure 7: Electric arc discharge reactor.

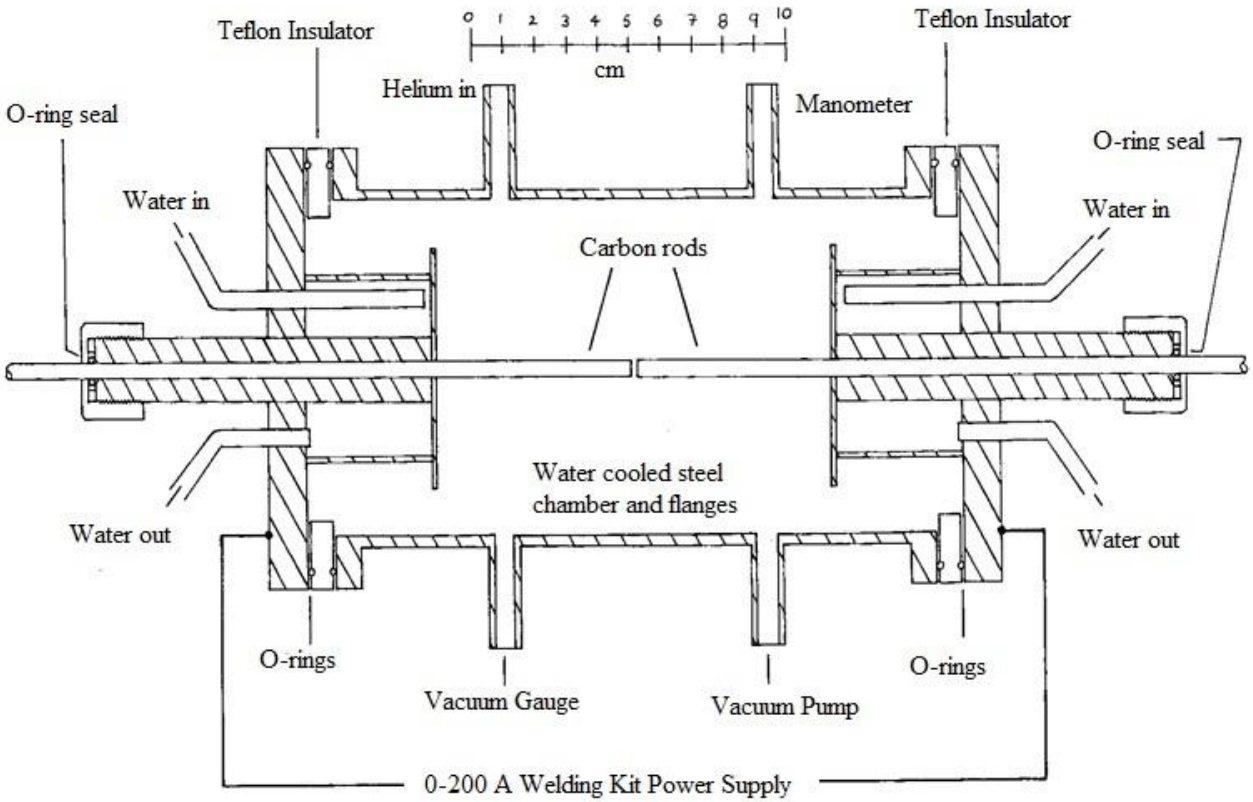

Figure 7: Electric arc discharge reactor [34]

5.1.2 Laser synthesis

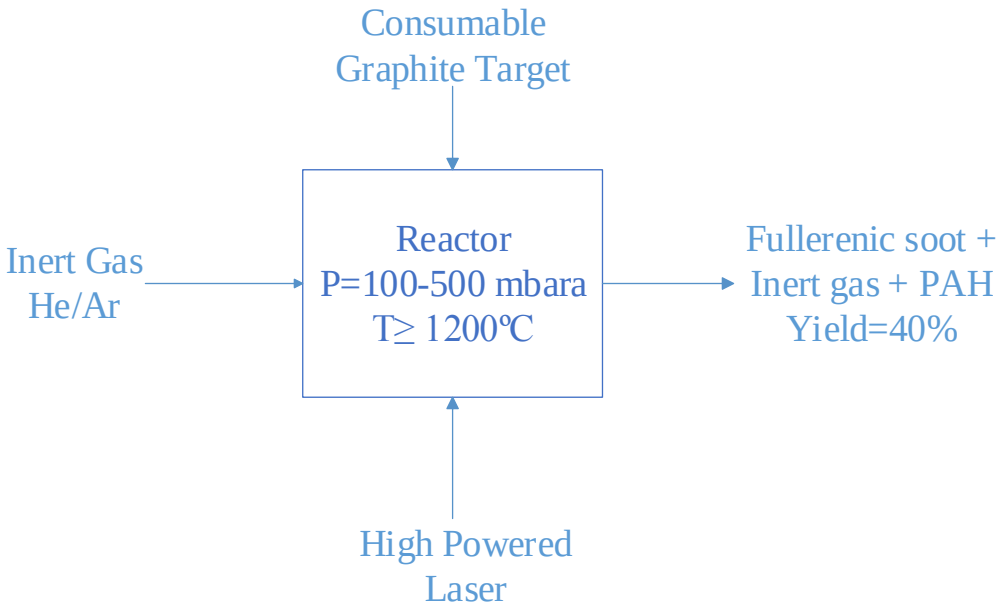

Figure 8: Laser synthesis block flow diagram

Laser synthesis was the first method used to produce fullerene synthetically. A high-power laser, converging lenses, sealed quartz chamber, vacuum pump, and a graphite target are the main requirements for this process. The graphite target is placed in the quartz chamber, and the air is removed using a vacuum pump. Helium or argon is used to maintain the pressure between 100-500 mbar absolute. The lenses are used to focus down the high-powered laser onto the graphite target. When the laser hits the target, it takes seconds for the graphite to heat up following which vaporization begins and the carbon vapor formed reacts to produce fullerenes. The soot is then scraped off and collected. This method

provides the highest yields of all methods ~40%; however, the production rates of fullerene are about 0.1 g/hr.

An illustration of the apparatus used by Iijima et al. is shown in Figure 9: Illustration of the apparatus used for laser ablation which shows the graphite target is heated to 1200 ^{0}C following which a laser is focused on the target and the fullerenes are collected at the exit of furnace along the walls on the right-hand side.

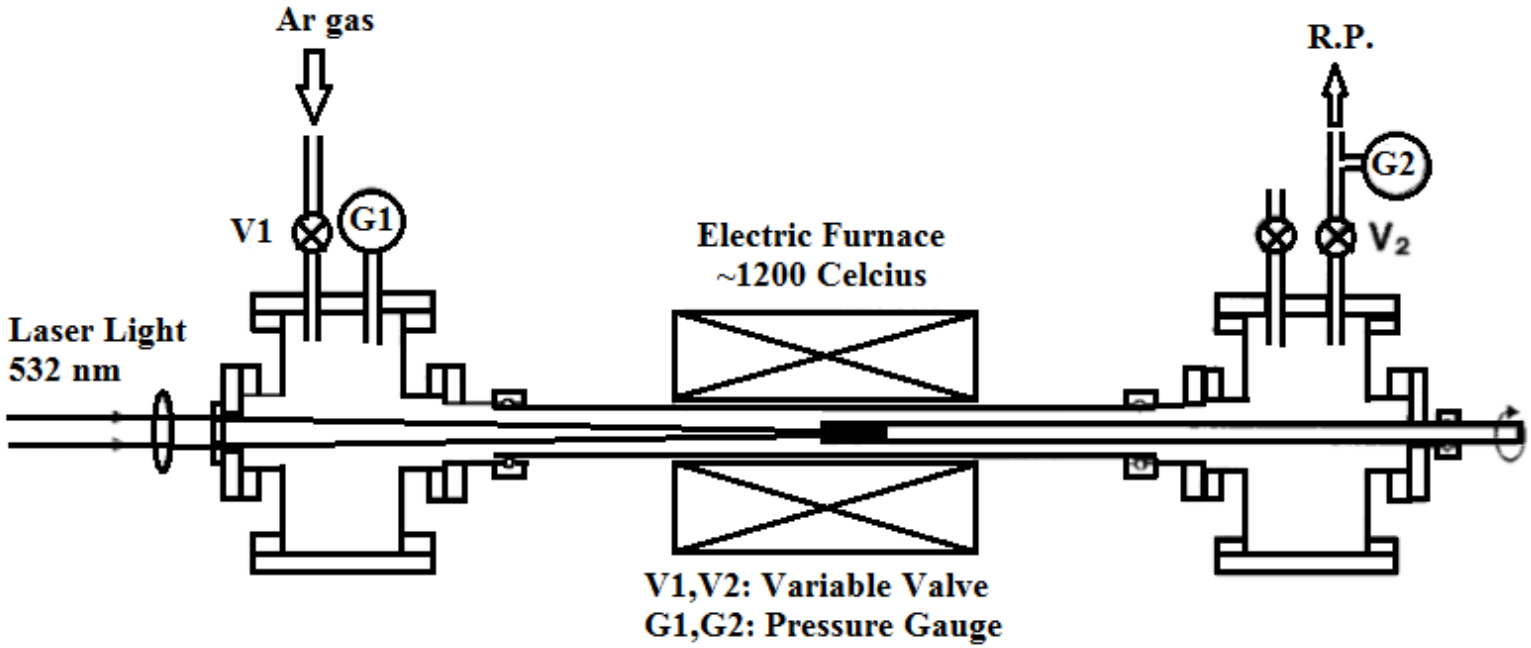

Figure 9: Illustration of the apparatus used for laser ablation [35]

5.1.3 Solar synthesis

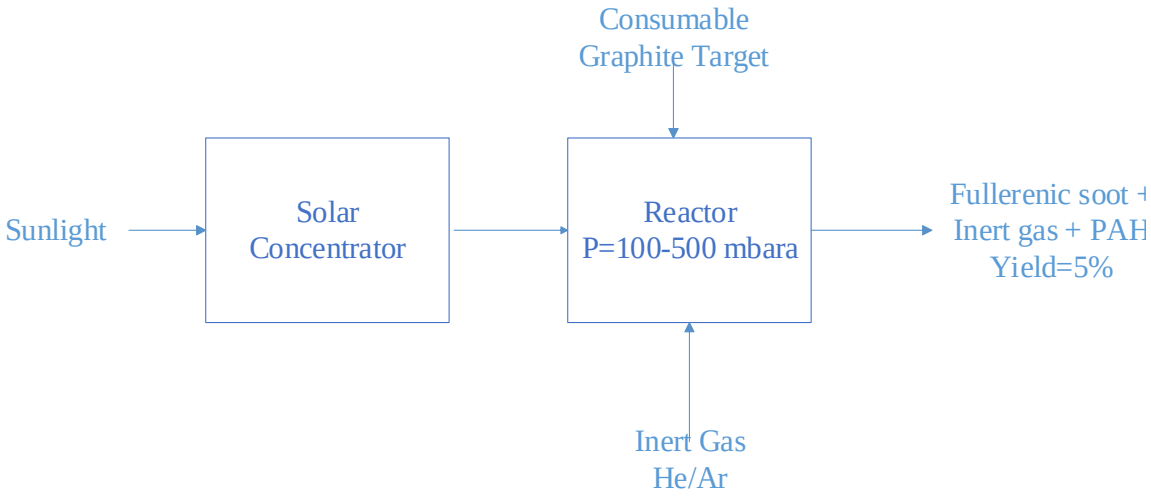

Figure 10: Solar synthesis block flow diagram

Solar energy has been powering life on earth for billions of years. On average, the earth's surface receives 1000W/m^2 of energy. With most methods for fullerene production having high energy costs, it only makes sense to try and use solar energy. To do so, researchers used various designs of solar flux concentrators that were then focused using lenses onto a graphite cylinder placed inside a quartz tube under an inert atmosphere. The graphite evaporates to form carbon vapor which in turn forms fullerenes. A yield of about 5% and a fullerene production rate of 20 g/hr is observed.

5.1.4 Combustion synthesis

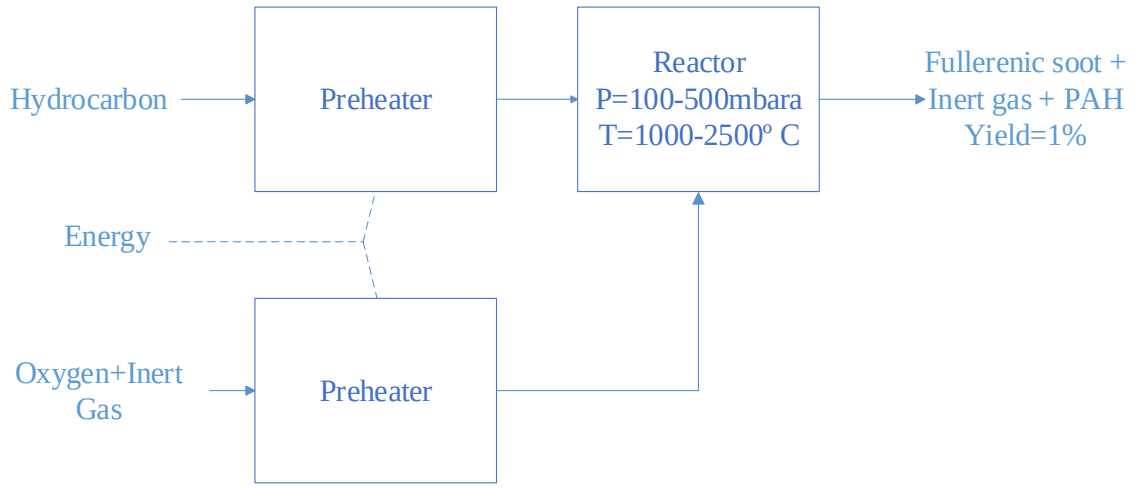

Figure 11: Combustion synthesis block flow diagram

The most popular method for commercial production of fullerenes is the combustion synthesis. The carbon source in this method is a hydrocarbon (mostly benzene or toluene), this undergoes incomplete combustion along with pure oxygen and an inert gas as a diluent in a fuel-rich environment to produce soot containing fullerenes. The heat from the combustion provides high enough temperatures for fullerenes to form and anneal. This process is similar to the soot produced in a flickering candle flame that produces soot. Numerous studies have been conducted and is the method used by frontier carbon (a leading fullerene manufacturer) for their 40-ton plant. The process produces ~10% soot of the total carbon feedstock at sub-atmospheric conditions. This soot has fullerene yield of ~10%, which is effectively ~1% of the total carbon feedstock.

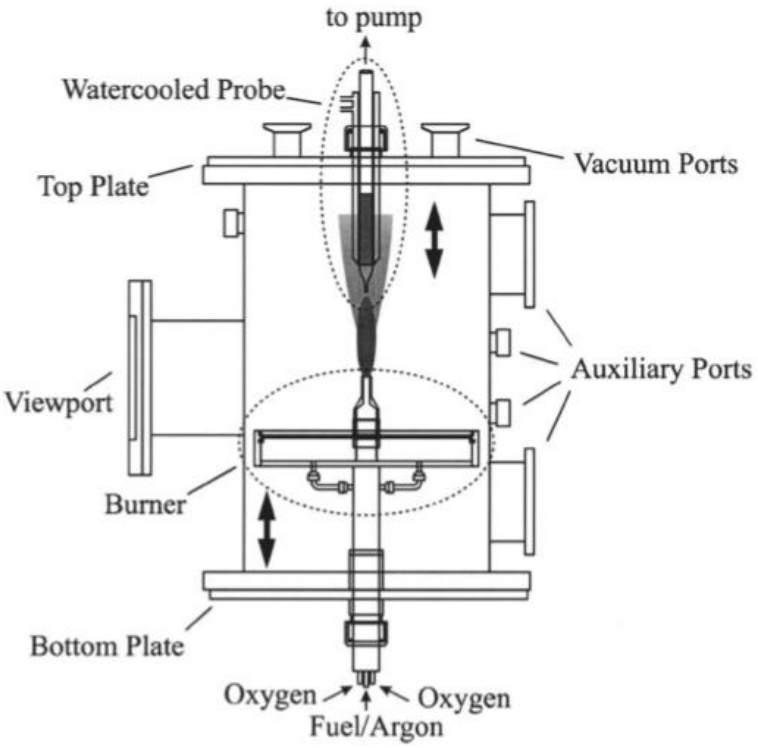

Figure 12: Typical combustion synthesis experimental setup [36]

The figure above (Figure 12: Typical combustion synthesis experimental setup) shows a typical set up for combustion used by Goel et al. The carbon source along with the oxygen and diluent enters from the bottom where it is premixed and injected to the flame using a nozzle. The water probe is connected to a filter followed by a vacuum pump which not only helps maintain pressure but also help remove the soot from the chamber to the filter. The various viewports are for diagnostics.

5.1.5 Plasma synthesis

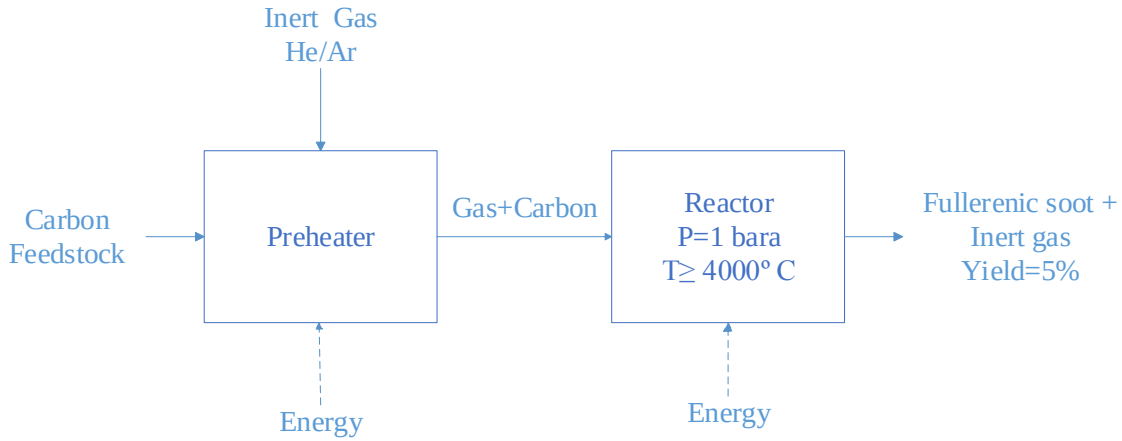

Figure 13: Plasma synthesis block flow diagram

A relatively new method for fullerene production is thermal plasma synthesis. This method production of high-temperature plasma (hot ionized gas like the sun) using either radiofrequency, induction, DC or AC power sources to serve as a heat source while using an inert gas such as helium or argon as plasma gas. The carbon feedstock can be either a hydrocarbon in the gas phase or carbon black as an aerosol. However, carbon black is more widely used. The carbon particle undergoes evaporation when it enters the hot plasma to form carbon vapor which then reacts to form fullerenes. This is a continuous process and has yields of about 5% with a production rate of about 150 g/hr.

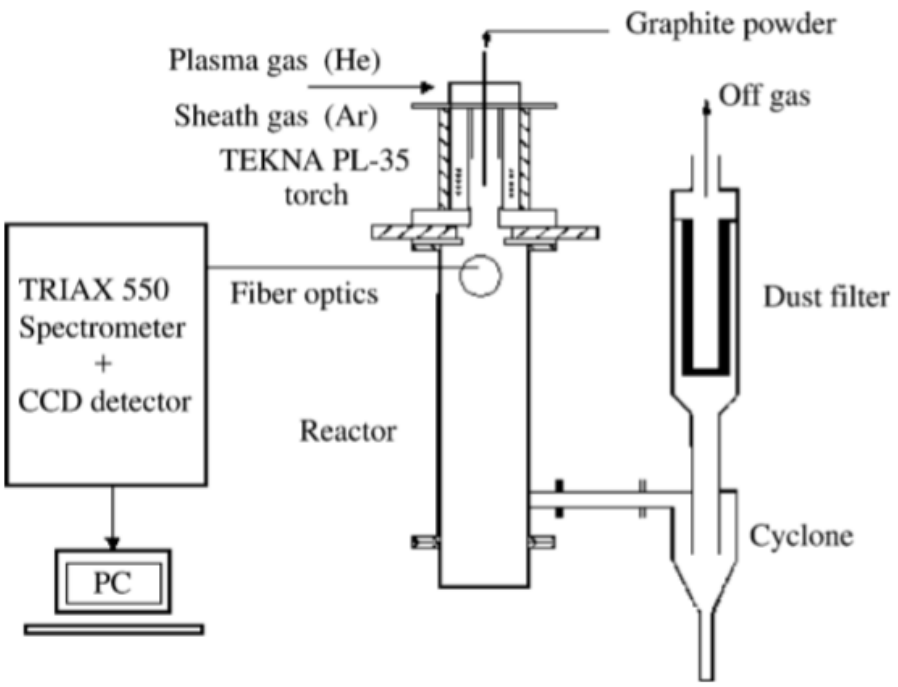

Figure 14: Plasma synthesis schematic

The above figure (Figure 14: Plasma synthesis schematic) is a good representation of the plasma synthesis process. It utilizes an off-the-shelf RF plasma torch from Tekna as the plasma source, graphite powder is injected from the top along with plasma gas into the plasma, and the products are collected either by using a filter and cyclone.

5.2 Growth mechanism of fullerenes

In properly designing a process to produce fullerene, it is important to understand the underlying mechanism behind it. There are multiple theories present; however, there is no definitive empirical data to establish a basis.

Fullerenes were discovered by Kroto, Smalley and Curl using laser vaporization of a graphite target. They postulated a mechanism known as the Party-line scheme: when carbon is in the vapor phase, it reacts to form dimers and trimers (C_2 and C_3) which come together to form linear species, which would then react with other linear species to make rings. Further addition of small linear chains would increase the size of the rings until they reached 25-35 atom range [38]. The mechanism assumes that in this size domain, polycyclic networks resemble open graphitic sheets as it is more thermodynamically stable. These sheets are hypothesized to be more reactive than rings or linear chains because they have more dangling bonds, to minimize these bonds, the network incorporates some pentagons causing curvature thereby reducing the number of edge dangling bonds which is thermodynamically favorable. Occasionally the networks incorporate enough pentagons in the right locations, forcing it to close into a hollow cage. This theory was developed when the fullerene yield was extremely low, and only microscopic quantities were produced. When yields of 20% and more were achieved, a new explanation was required.

Smalley and coworkers modified their original party line mechanism and named it the pentagon road.

Three assumptions were made for the lowest-energy form of a small graphitic fragment

1) The fragment is made up of only hexagons and pentagons
2) The fragment shall have as many pentagons as possible

3) None of the pentagons will be adjacent

The pentagon road also proposes that carbon networks with 20-30 atoms which are too small to form a fullerene molecule with isolated pentagons have the lowest energy. In slow cooling or annealing environments, the thermochemical stability dictates the formation of curved graphitic cups by allowing carbon structures to find a structure with minimum energy. [39] [40] The main concept behind the pentagon road is the addition of C_2 and C_3 to the reactive edges of these cups until they form a fullerene molecule with no dangling bonds thereby ending the reaction. There are multiple modifications or additions made to this mechanism, however, the most promising one seems to be based on quantum chemical dynamics.

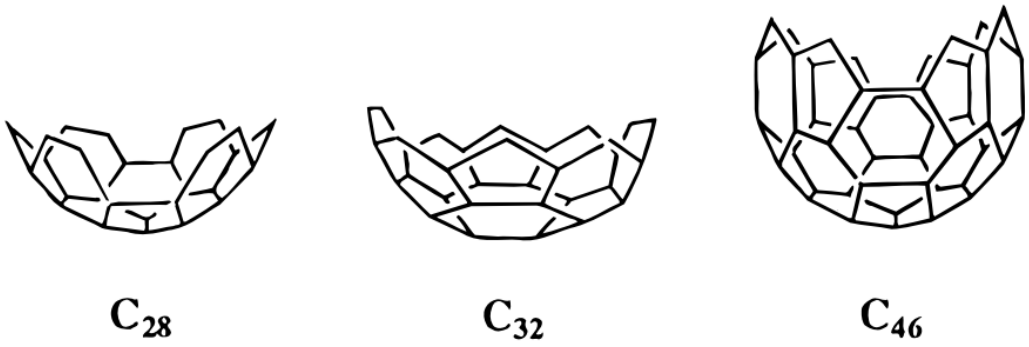

Figure 15: Hypothetical intermediates along the Pentagon road [39]

This new theory is based on the study of nonlinear dynamics which tells us that a system can evolve to a steady state even if it is far from equilibrium. This is contrary to the other theories which obey the laws of classical thermodynamics emphasizing the importance of equilibrium structures such as crystals [41]. According to this theory, C2 is the building block; it starts with the nucleation phase where C2 radicals interact with each

other to form small linear chains which then interact with each other to form monocyclic ring structures such as triangles, quadrangles or pentagons. Next is the ring condensation phase where multiple rings come together to form a condensed ring. Once this number is large enough, the structure starts to close. As long as there are C2 radicals available the structure grows by the addition of C2 to the structure to form larger structures. Not all of these structures are stable. Thus if an unstable structure is formed and no new C2 radicals are available, it simply loses the C2 until it reaches a thermodynamically stable structure. [42] [43] [44] [45].

The growth of structures can be controlled by limiting the amount of C2 radicals; this can be achieved by reducing the temperature. This is done by either changing volume or pressure in the system or in other words by quenching the reaction.

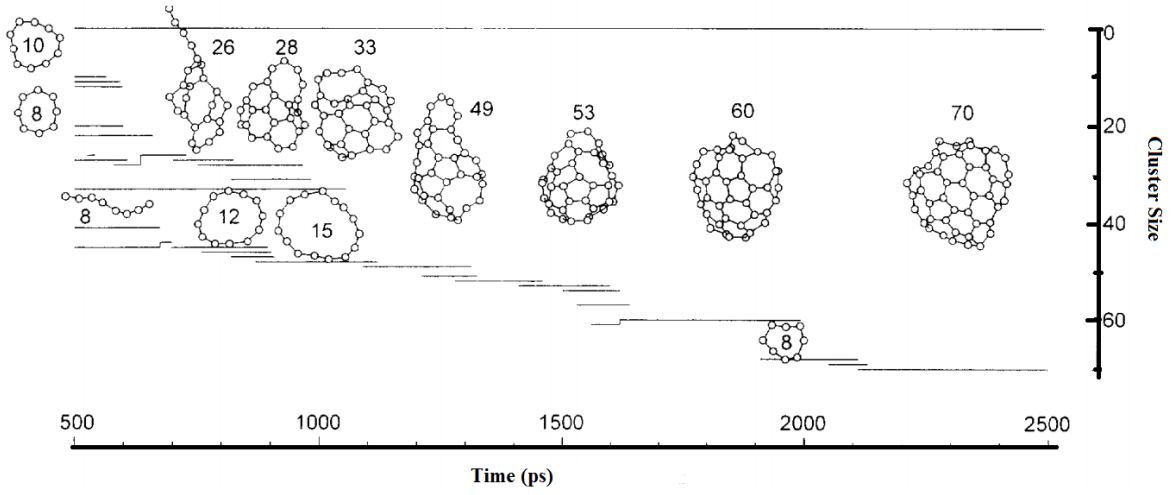

Figure 16: A dynamic path to C60 and C70

5.3 Evaluation of synthesis methods

A summary of various fullerene production processes reviewed in Appendix A is presented in Table 1 **[46]**. The electric arc production processes are given in Table 2, while the laser synthesis processes are in Table 3. The solar synthesis processes are in Table 4 while the combustion processes are in Table 5. Lastly, plasma synthesis processes are reviewed in Table 6.

The applications for fullerenes range from nano-sensors to organic solar cells and from drug delivery to cosmetics and medicine. These require a process capable of producing high purity fullerenes in the tons/day quantities in order to realize the true potential of this unique and novel nanomaterial.

The commercialization of fullerene processing technologies has been inhibited by two main factors a) high selling price of pure fullerenes b) lack of a reliable, scalable and efficient production process. Consequently, the commercial use of fullerene in potential applications is highly dependent on the development of a low cost, continuous, environmentally friendly, high throughput, and commercially scalable fullerene production process.

The criteria for selecting a scalable production process include capital and operating costs, raw material selection, operation mode, environmental concerns, safety, and bulk production and post-synthesis purification requirements. The process operating conditions such as reactant yield, process type, and gas requirements are also considered for selecting the appropriate technology.

Table 1: Evaluation of fullerene synthesis methods

Process	**Principle**	**Continuous/ Batch**	**Fullerene yield (in soot)**	**Upscaling**
Arc	Ablation of C rod using an electric Arc	Batch	10% (pilot)	No (UV destruction)
Laser	Ablation of C rod under a Laser beam	Batch	40 % (Lab)	No (power limitation + Cost)
Solar	Ablation of C rod under focused sunlight	Batch	5 %	Yes (power limitation + Cost)
Combustion	Incomplete combustion of hydrocarbon	Continuous	5 %	Yes (Envir. + Feedstock Cost)
Plasma	Treatment of C powder by arc plasma	Continuous	5 % (pilot)	Yes

Table 2: Evaluation of electric arc discharge synthesis methods

Reactor MOC	Power	Gas	Pressure (absolute)	Carbon source	Process	Yield	Literature
Stainless Steel	150 A DC	He/Ar	100-200 torr	Graphite electrode	Batch	3-15%	Haufler et al, 1991
Stainless Steel	45-100 A	He	100 torr	Graphite electrode	Batch	1-32%	Sesli et al, 2005
Stainless steel	150 A dc	He	200 torr	Graphite electrode	Batch	6%	Kyesmen et al.,2016
Stainless Steel	100-150 A dc	He	100-200 torr	Graphite electrode	Batch	6-8%	Onoja et al., 2015

Table 3: Evaluation of laser synthesis methods

Reactor MOC	Gas	Laser	Carbon Source	Pressure (absolute)	Yield or production rate	Literature
Glass		CO_2 laser, CILAS CI 1000 & PRC-Oerlikon 1500	Ethylene, acetylene, and benzene	166-760 torr	0.02-1%	Armand et al., 1997
Quartz tube	Ar	Cw-Nd-YAG laser (NEC SL116D) & Q-switched pulsed Nd: YAG laser (Continuum Powerlite 9010)	Graphite rod	150-802 torr	0.05-0.8mg/hr	Oyama et al., 1997
Plastic Resin Chamber	He/Ar/ N2	20 kW/cm^2 CO_2 laser	Graphite rod	150-760 torr	0.1-4%	Kasuya et al, 2001

Table 4: Evaluation of solar synthesis methods

Solar Density	Solar Power	Pressure (absolute)	Soot Production	Yield	Literature
7-8 kW/m^2	50 kW	Not stated	3.6-14.4 g/hr	5%	Flamant et al, 2004
900 W/m^2	Not stated	50 torr	1.6 mg/hr	Trace	Chibante et al, 1993
2000 W/m^2	Not stated	50 torr	Not stated	Not determined	Fields et al., 1993

Table 5: Evaluation of combustion synthesis methods

Fuel	**Pressure (absolute)**	**Soot Production**	**Yield**	**Literature**
Benzene	20 torr	2-3%	~7%	Goel et al, 2002
Toluene	40 torr	~10%	~10%	Takehara et al, 2005
1,2,3,4 tetrahydronaphthalene	40 torr	~8%	~2.25%	Alford et al, 2008
Benzene	100 torr	0.0026-9.2%	0.26%	Howard et al, 1992

Table 6: Evaluation of plasma synthesis methods

Reactor power	Plasma Type	Feedstock	Total gas flow rate	Feed rate	Yield	Literature
27 kW	RF	Graphite	55-67 slpm	156 g/hr	4.1%	Todorovic-markovic et al, 2003
30 kW	RF	<20um graphite	150 slpm	5 g/hr	-	Wang et al., 2001
30 W	High-Frequency Thermal	Acetylene	10250 l/hr	250 l/hr	2.5 g/hr	Chen et al., 2002
12 kW	Plasmatron	Acetylene black	18-20 slpm	200 mg/min	2%	Dubrovsky et al,2004
36 kW 180 A, 150 V	3-phase AC	Carbon black	208,000 l/hr	800 g/hr	0.962%	Fabry et al, 2016
19 kW 220 A, 80 V	3-phase AC	Acetylene black	210000-235000 l/hr	200-600 g/hr	4.5%	Fulcheri et al, 2012
100 kW	3-phase AC	Acetylene black, graphite, carbon black and cokes	30-80 slpm+ quench gas	0.5-1.5 kg/hr	3.58%	Fulcheri et al, 2000

Operating conditions such as pressure and gas requirements play a vital role in determining the scalability of a production process economically. Working above or below atmospheric pressure would not only require more expensive and precise machining but also adds costs of compressors or vacuum pumps and requires a more complex process control system with added safety costs. The type of gas and its flow rates would directly affect the operating expenses of a plant and would be directly responsible for the production costs of the product. Using helium instead of argon or nitrogen would be more expensive as helium is mined, and helium reserves are dropping worldwide, the flow rates and purity required would determine if recycling is possible and if it is economically viable. The reactor yield and production rates would help determine the extent of reaction and process scalability. High yields at high production rates would decrease the energy utilization per unit product and would be ideal. The commercial scalability of the arc and laser processes have been limited so far in terms of production capacity, ease and cost of production, and scale–up constraints. They are batch processes.

Solar processes have a relatively high yield but have been limited so far in terms of production capacity, ease and cost of production, scale-up constraints, and elaborate setups. The high energy constraints and low throughput inhibit scalability commercially. It appears the economical limit for scaling up these processes has been reached, with production rates of 1 g/hr of raw fullerene soot (unreacted carbon+ fullerene).

An analysis of the combustion process reviewed based on criteria such as feedstock, gas requirements, pressure, sooting percentage and yields showed that the combustion processes provide a commercial basis for conceptual design of a scalable fullerene production process. The combustion process uses readily available organic solvents as

feedstock, some of them use inert argon as a diluent but the requirements are quite low, and they don't require helium which is more expensive. The amount of soot produced is between 8-10% which is an acceptable amount with good yields of 10%. It is a continuous process and is a net producer of energy which is a big advantage over the other batch processes.

Organic solvents are carcinogenic and as they undergo incomplete combustion >90% of these solvents either convert to CO, CO_2 or polyaromatic hydrocarbons. The combustion process is the process of choice for current manufacturers, and the technology seems to be working at its best efficiency with little to no scope for improvement thereby leading to stagnation in prices. With the new carbon tax in Canada in place and environmental concerns with these greenhouse gases, suggest production costs will only increase.

The soot produced by combustion has high quantities of PAH and amorphous carbon which get intercalated in the fullerene structures and are detected in fullerenes even after purification and is a concern if these fullerenes are to be used for health and medicine.

Another alternative to the combustion process is plasma synthesis of fullerenes. Plasma synthesis mainly uses solid carbon as feedstock thereby eliminating the possibility of solvent trapped fullerene which is perfect for high purity applications. It is a continuous process and has good yields of about 3-5%. At first glance these yields might appear to be lower than the 10% of combustion process however 90% of the feedstock in the combustion process is lost as greenhouse gases (CO and CO_2) and the non-fullerenic soot left behind after fullerene extraction is a waste by-product needing disposal while in plasma synthesis process after removal of 3-5% fullerenes the unreacted feedstock can be recycled

right back into the reactor thereby giving the process a 100% conversion rate effectively(after multiple passes). This helps in lowering the feedstock costs.

Plasma torches are being used for multiple applications from nanoparticle synthesis to waste remediation; it is a proven technology and can be scaled up to any desired size. Fullerene production using plasma has also been proven at different scales right from 12-100 kW. They have the highest fullerene production rate of all the processes available. They do have a big drawback of using large quantities of helium which can be resolved by using a recycling system or better still by designing a new reactor to reduce the gas consumption keeping the yields in the same regime. The lack of greenhouse gas emissions should ensure no added costs once the carbon tax is implemented worldwide and the possibility of recycling should allow the costs to be lowered below the current levels.

Plasma can be formed using RF, high voltage, DC or AC power sources. These are evaluated based on ease of operation, power supply cost, and complexity, plasma stability, plasma quality, and scalability.

High voltage thermal plasma is easy to operate, and the power supply is straightforward to design; however, it has relatively low currents which make for a low energy plasma. This limits vaporization of the carbon thereby limiting fullerene formation. If a high current high voltage power supply were to be used it would be extremely expensive as well as increasing safety concerns. Scaling would not be easy with this plasma.

RF and DC plasmas are well researched and have complex power supplies; they are expensive as they require high current frequency modulators or rectifiers to convert AC to DC power. Since high currents are used, line losses with DC are extremely high and affect

the efficiency of the power supply. Stability of DC plasma is also a concern with solid feedstock, and it is determined that plasma quality is not great. While RF plasma is stable, with solid feedstock, it is not able to achieve high energy plasmas efficiently.

AC power torches have a complex design; however, the power supply costs are lower with high power factors. The plasma torch is stable and can sustain high-temperature plasmas. Scaling is not a problem and is already demonstrated for various applications such as waste remediation. It is currently used with high gas flow rates, but a new design of the torch with a low gas consumption should be possible. Consequently, an AC plasma can sustain a high-temperature plasma, has low power losses, is easy to operate and is scalable. It needs some work with the gas flow rates to improve efficiency as lowering the gas flowrate would not only reduce recycling loads but would also make the reactor more efficient by reducing the temperature gradient across the reactor thereby allowing more time for the fullerenes to anneal.

Fullerenes formed with a 3-phase AC plasma can be recovered solvent-free, and the unreacted carbon can be recycled. The gas used is helium or argon which can be recycled since there should be little to no PAH production, the power supply should be easy to design as scalability is already proven and plasma stability and quality are perfect for fullerene production. This process seems to be the most promising for commercialization and should be able to achieve a drop in fullerene prices with efficient use of the reactor. It would provide solvent free soot which can then undergo further processing to ideally yield solvent free pure fullerenes.

The purification of this soot and the various processes currently available shall be reviewed in the next section, followed by an evaluation to design an ideal process.

5.4 Extraction of soot

Fullerenes, as produced by different synthesis processes, contain impurities such as unreacted feedstock, amorphous carbon and polyaromatic hydrocarbons (PAH). These impurities must be removed before the fullerene can be used for any application. Consequently, a couple of extraction methods have been devised to improve the purity of the fullerenes produced. The extraction methods employed in post-synthesis processing of fullerenes are divided into two main categories Solvent extraction and Sublimation. A detailed literature review of these methods is presented in this section.

5.4.1 Solvent extraction

This is the oldest and primarily used method for soot purification. There are multiple techniques using solvents to extract soot efficiently, however, they all are based on the use of an organic solvent which can dissolve fullerenes, thereby separating them from the unreacted carbon, followed by solvent evaporation to produce a mixed fullerene extract. Further purification by chromatography or selective adsorption on activated carbon can be done.

These techniques are well understood and developed. They work well with soot produced using combustion synthesis because the soot already contains PAH's, unreacted organics and trapped feedstock. The extract obtained by this method contains trace amounts of solvents which isn't desirable in most applications. The unreacted carbon is also not used for anything and may be sold for other applications or sent to the landfill. The

solubility of fullerenes in solvents is low, and one needs to use 1700 barrels of solvent for every ton of fullerene. It is time-consuming.

Several different extractions and purification procedures and conditions are reviewed below.

Chatterjee Kuntal, et al., "Fast one step separation and purification of buckminsterfullerene, C60, from carbon soot", Journal of Organic Chemistry, 1992, 57, 3253-3254 [47]

This method used a Kauffman apparatus to combine the efficiency of a Soxhlet extraction with a selectivity of a chromatographic column for a one-step method.

1) Aluminum oxide is loaded in the inner column of the apparatus, and a small amount of raw soot is placed on top.
2) The alumina is held in place by a porosity B frit at the bottom and to prevent the soot from flying due to air currents or static charge some additional alumina is added on top of the soot.
3) The inner and outer columns are attached and fitted with a condenser which is placed above a pre-weighed flask of hexane.
4) Once reflux begins, the solvent vapors from the boiling flask rise through the space between the inner and outer columns and continue through the holes near the top of the inner column into the condenser. The condensate then falls onto the raw soot, extracts the fullerenes, and passes through the alumina column. The violet C60 band is readily separated from the band containing

C70. Hexane and the purified C60 flows into the boiling flask, and hexane is again vaporized while the purified C60 remains in the flask.

The apparatus needed 250 ml of hexane to obtain 0.268g from 4.5 g of soot over 200 g of alumina.

Komatsu Naoki et al., "A highly improved method for purification of fullerenes applicable to large scale production", Carbon 42(2004) 163-167 [48]

Activated charcoal is cheap and commonly used in many adsorption applications. Using activated charcoal for fullerene separation is not advisable as it undergoes irreversible adsorption and almost all C_{70} and highers (C_{76}, C_{78}, C_{84}, and other higher fullerenes) are lost.

1) A slurry of powdered activated carbon in toluene (15g in 150 ml) is filtered under reduced pressure through a Buchner funnel (70 mm diameter) to form a flat activated carbon layer (15mm in thickness) on the filter paper.

2) A fullerene and toluene solution (1.85g in 400ml) is filtered through the carbon layer under reduced pressure

3) Successively, additional toluene (1L) is passed through the carbon bed at a rate of 180ml/min to elute the adsorbed C60.

4) The deep violet filtrate (1.4L) obtained is concentrated using a rotary evaporator, and the residue is dried using a vacuum to give C60 (1.2g).

5) Yield of over 90% is achieved.

Jinno Kiyokatsu et al., "Subcritical Fluid extraction and supercritical fluid chromatography of carbon clusters C60 and C70", Journal of Analytical Chemistry (1992) 344,435-441. [49]

This method uses a 1:1 mixture of toluene and subcritical CO_2 at a total flow rate of 1ml/min at 100°C and 250 bar pressure. It was determined that this method was very efficient in removing fullerenes from the surface of the soot and not from the bulk because C_{84} and larger members of the fullerene family) the fluid cannot penetrate the bulk. The fluid only extracts C_{60} and C_{70}, and highers (C_{76}, C_{84}) are lost. The total soot used in this method is 100 mg and requires large quantities of solvent like the Soxhlet extraction. However, the total process of fractionation of fullerenes is much simpler and needs to be tested and automated on a pilot scale for further testing.

5.4.2 Sublimation

Fullerenes start to vaporize $>500^0$C at atmospheric pressure. Fullerenic soot obtained from all other techniques apart from combustion does not contain trapped solvent as the feedstock is either a piece or graphite or powdered graphite/carbon black. This soot can be separated from the unreacted carbon by subliming the fullerenes. The sublimed fullerene can either be collected all in one spot or can be collected over a temperature gradient which will provide a crude separation of the fullerenes. This separation would be solvent free, and the unreacted carbon can be recycled back as feed, while the separated fullerenes can then either be used as is or can be further purified.

Chahan Yeretzian et al., "Partial Separation of Fullerenes by Gradient Sublimation", Journal of physical chemistry, 1993, 97, 10097-10101. [50]

1) 400 mg of fullerene-containing soot is placed at the closed end of a 12-inch long quartz tube (3/4 inch diameter).

2) The tube is evacuated to 1 mtorr absolute and is sealed.

3) This is then introduced in a resistively heated temperature-controlled furnace kept at 1050 °C, the end containing the soot resides in the hot region of the furnace whereas the other side containing a Teflon seal is placed outside at 100 °C to create a temperature gradient.

Fullerenes are sublimed and deposited on the tube. It was determined that fullerenes with a lower sublimation temperature were carried further than those with a high sublimation temperature. Using laser desorption it was determined that one could obtain three bands of fullerenes with 1) pure C_{60}, 2) C_{60}+C_{70} mixture 1:1 and 3) C_{70}:C_{60}>1.

5.5 Evaluation of extraction methods

The review of various extraction process showed a primarily solvent-based technique for the extraction of fullerenes from soot. Typically, the soot is mixed with a solvent and undergoes extraction. However, the initial tests for sublimation provide exciting results for the solvent-free separation of fullerenes using a simple process.

Sublimation is the only solvent-free technique which can be used to produce ultra-pure fullerenes from a solvent-free production process.

5.6 Summary

The various fullerene synthesis techniques and post-synthesis extraction processes have been reviewed in this chapter. The most frequently used methods for fullerene production rely on the production of C_2, C_3 dimers, and trimmers which condense to form fullerenes. The production processes reviewed are batch processes and are in the grams/day scale. However, fullerenes require a production capacity of a couple of kgs to tons/day based on market projections. Consequently, the development of a large volume, commercially viable fullerene process is essential to maximize the potential and benefits of these nanomaterials. Furthermore, many applications require high purity fullerenes. The fullerenes produced by all processes contain impurities such as amorphous carbon, unreacted feedstock and PAHs which need removal. The main factor for the selection of any post-synthesis extraction process should be the removal of the impurities without the use of any organic solvent.

Industry currently uses combustion followed by Soxhlet extraction to recover mixed fullerene extract which is further purified using chromatography and lastly

sublimation is used to obtain ultrapure fullerenes. Each step of the way fullerene is lost which adds to the cost of fullerene production. The

Figure 17: Current Industry Process block flow diagram. Assuming a 1000kg/hr of carbon input in the form of a hydrocarbon at the best efficiencies of 10% soot containing 10% fullerene, we get about 10g/hr of fullerene produced. This is then dissolved in toluene and undergoes Soxhlet extraction at 90% efficiency. The 9 g/hr of extract from the Soxhlet extraction process is then dissolved in solvents to run through a chromatography column to separate C_{60} from the other fullerenes this normally occurs at 60-90% efficiency depending on the stationary and mobile phase. Assuming 90% efficiency, we are left with 8.1 g/hr of fullerenes in total. This is 99.99% pure, however, it still has substantial solvent remaining, which is unsuitable for use in the health/electronic industry. This material now undergoes sublimation leaving us with net 8.1 g/hr of sublimed separated fullerene. The multiple steps and losses along with low production rates are the primary reason for the high prices of fullerenes. Even if one were to skip Soxhlet extraction and chromatography and jump straight to sublimation the sublimed material would still have traces of solvent/PAH thus limiting the sublimation efficiency. This cannot be avoided as it is a part of the production process in combustion synthesis, however, it would reduce costs, and the product would be a better comparison to our product. This block flow diagram is shown in

Figure 18: Combustion process with direct sublimation.

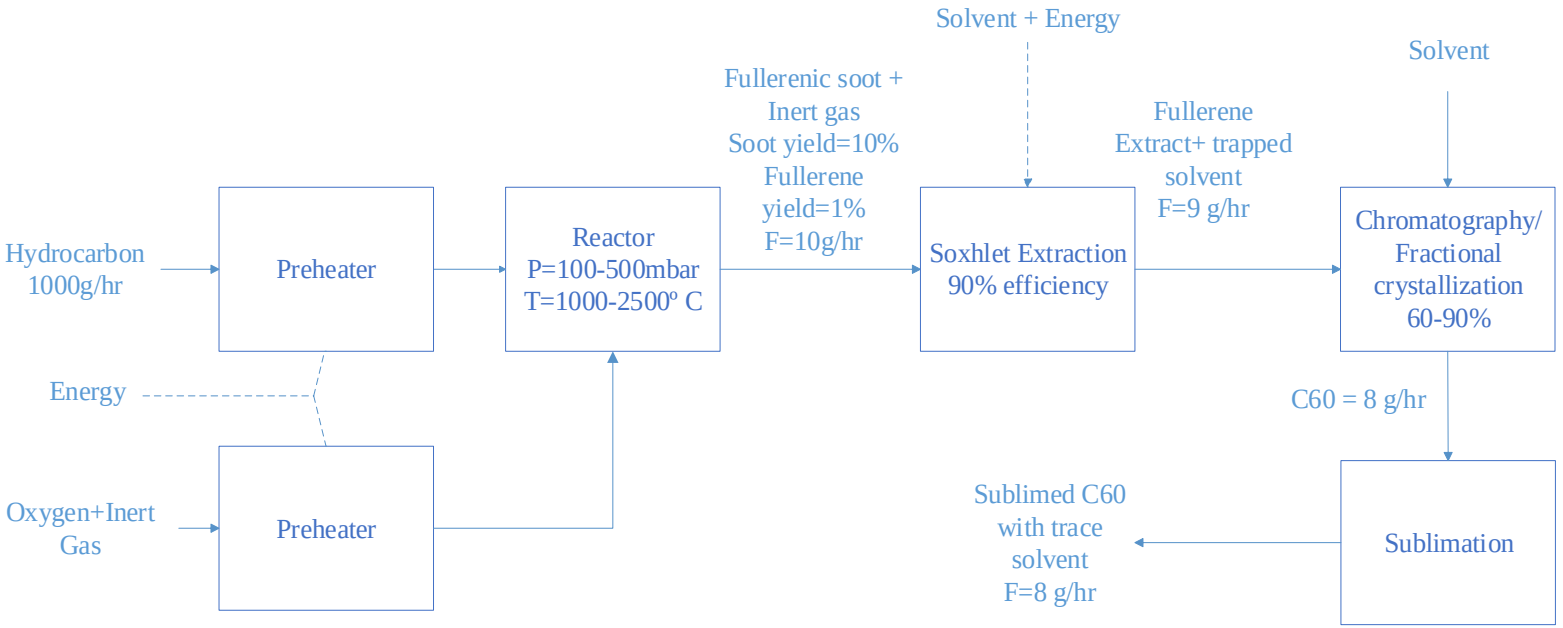

Figure 17: Current Industry Process block flow diagram

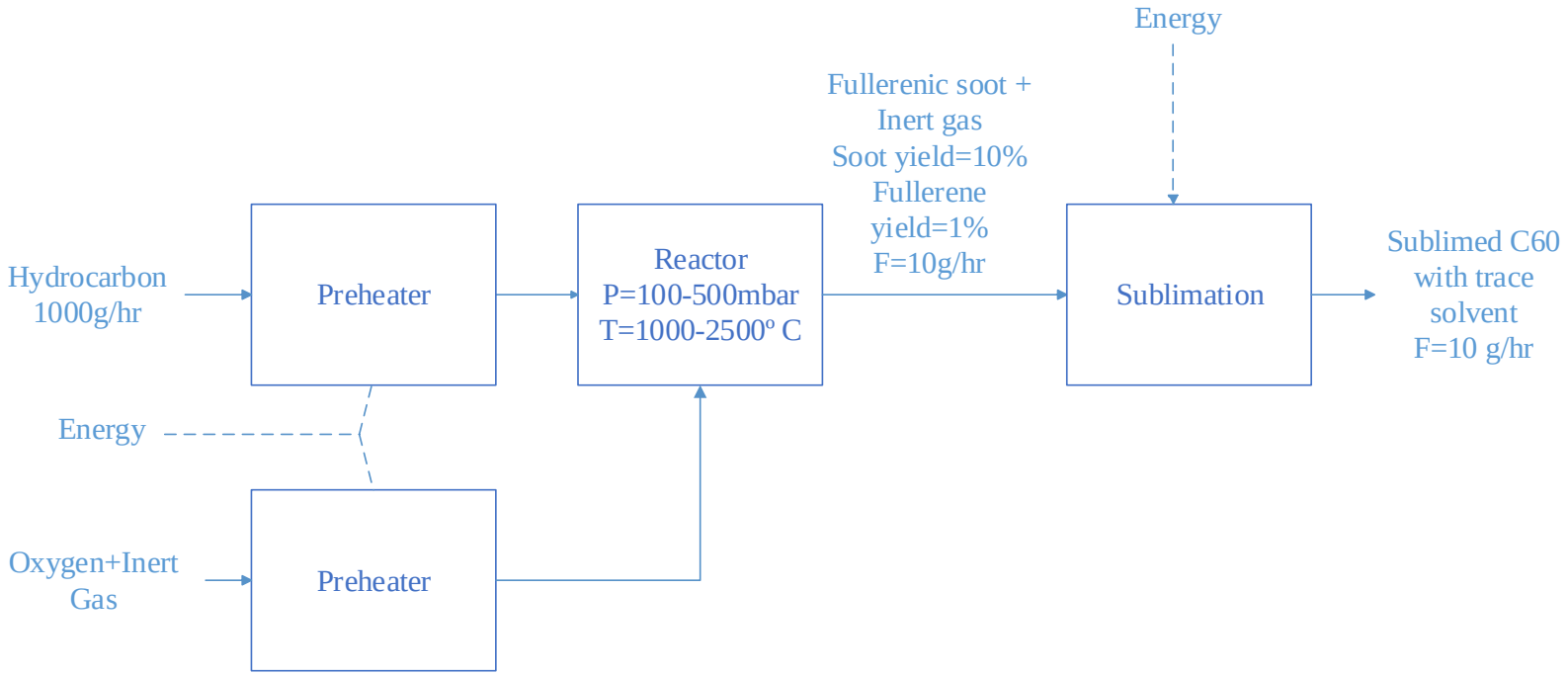

Figure 18: Combustion process with direct sublimation

In comparison, the AC 3-phase plasma synthesis process may be the most promising process used as a basis for scale-up. This thermal process is continuous, solvent-free, green, high throughput, high yields and safe. The proposed process is presented in the block flow diagram in

Figure 19: Block flow diagram of proposed process. The reactor development shall be discussed in the next chapter.

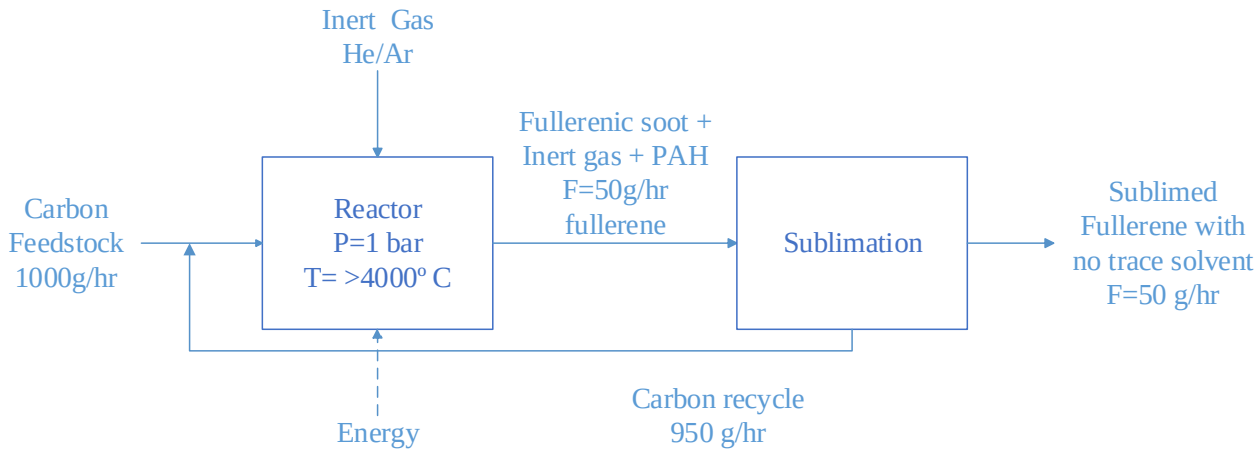

Figure 19: Block flow diagram of proposed process

Purification by sublimation seems like the only viable choice for purification. The sublimation unit can be online or offline depending on the conditions necessary. Further work needs to be done to develop a purification process; it requires a proof of concept before it is tested on the pilot scale.

6 Research hypotheses

The design of a green economically viable process for fullerene production is the primary objective of this research. To achieve this the main question that needs to be addressed is whether a 3-phase plasma reactor can be designed that uses limited resources, is environmentally friendly, and economical to build and operate? To do so, we would need a stable thermal plasma reactor to run continuously with high efficiency. There are various parameters that play a vital role in plasma stability, namely: electrical power, ionization potentials of the plasma gas, gas purity and flowrates, carbon purity and flowrates. The effects of these parameters on plasma stability would need to be determined.

Electrical power is a key parameter to ensure plasma sustainability. Useable power composes of three main parts voltage, current and power factor. As long as the applied voltage is greater than the breakdown voltage of the plasma gas, a spark would be initiated, and the plasma state maintained. Current determines the temperature of the plasma, the higher the current, the hotter the plasma, since carbon evaporates >4,000 K the more the current, the better the evaporation. Power factor is another important factor in ensuring that all the power consumed by the system is being delivered to the plasma, idealistically a power factor of 1 is desired to have minimal losses. Overall, the increase in power plasma stability is expected to increase production.

Helium, argon, and nitrogen are common plasma gasses used in electrical plasma torches. Helium has the highest ionization potential and the hottest plasma (10,000-15,000 K). The plasma is violent, but with a well-designed system should be able to improve evaporation efficiencies while keeping the plasma stable. Argon and nitrogen have similar

ionization potentials that are lower than helium and hence result in a colder plasma (5,000-7,000K) but still relatively stable, so it could be a good option for plasma gas. Nitrogen, however, results in intermediate radicals that react with the carbon to form CN as an impurity which is undesirable. Helium is expected to be the best plasma gas for maximum carbon evaporation, but argon tests shall be conducted. Helium is expensive, and its reserves are depleting.

The plasma volume and temperature are also dependent on the gas flowrates. The plasma volume is expected to increase with the increase in gas flow rates, but the temperature is expected to decrease because now there is more gas to heat up per unit of energy being delivered to the plasma. Carbon flowrate would determine evaporation (carbon vapour concentration) and the overall temperature & stability of the plasma, the rate of evaporation is expected to increase until the energy needed for evaporation of carbon and heating of the gas equals the delivered plasma energy once the flow rate passes this point it would result in a drop in plasma temperature and possibly extinguishing the plasma thus decreasing the overall evaporation of carbon resulting in a decrease in fullerene formation.

Carbon and gas purity would be another parameter of key importance as with the increase in purity the feedstock costs rise exponentially. Hence, an ideal purity level would need to be determined to be the most economical. It is expected that with the increase in purity the yield should go up as none of the carbon vapour atoms are lost to reactions with the impurities.

Reactor design, electrode design, automation and the design of the solvent-free purification system would be other key aspects that would need to be done with experiential learning to ensure the success of the project.

Sublimation of fullerene-containing soot would need to be tested in both online and offline configurations. It is expected that offline configuration would work better as we can isolate and optimize the conditions for production and purification. A proof of concept for both should be demonstrated before a pilot scale system is designed and tested.

7 Reactor development

The Applied Nanotechnology Laboratory at the University of New Brunswick has designed their first-generation plasma reactor, Mark I. This chapter provides insight into the reactor re-designs from Mark I to Mark IV which is the final test reactor for this research.

7.1 Mark I

This reactor features off the shelf arc welding power supplies and has 3-zones namely, reaction, annealing, and quenching.

The process starts by ignition using a high voltage ignition arc at graphite electrodes leading to plasma production, this is followed by the introduction of carbon feedstock which vaporizes in the plasma forming carbon ion clusters. These clusters then move to the reaction zone where the carbon ions reassemble to produce fullerenes. Fullerenes are then annealed followed by quenching in the quenching zone where the reaction is completed, and fullerenes change form from vapor to solid. This is then collected and tested for yield. The key features of this design include the modular reaction zone and off the shelf power supplies. The initial design of Mark 1 and preliminary results are reported in the thesis "Novel Plasma Processes for Nanocarbon Synthesis" by Khosro Seddighi, a former member of the ANL@UNB [51].

7.1.1 Power supply

The power supply has two parts to it, namely the ignition system and the electrode power supply.

7.1.1.1 Ignition system

Plasma is essentially hot ionized gas which needs to be produced when and where it is needed. It cannot be stored or transported. One method of producing plasma is using a high voltage electric spark like that of a lightning bolt. When huge amounts of static charge build up in the atmosphere, it produces a large electric potential. Once this is large enough to overcome the breakdown/ barrier voltage of the gas a spontaneous electrostatic discharge occurs, this ionizes the gases producing a plasma which we call lightning.

Using the same concept, a high voltage DC power supply by Glassman High Voltage INC, serial: M9201955-01AP001013, model no. PS/EW20P30 is used to initiate the plasma. This power supply can supply up to 20 kV and 30 mA. The breakdown voltage of helium (the carrier gas used) is ~1500 V/cm.

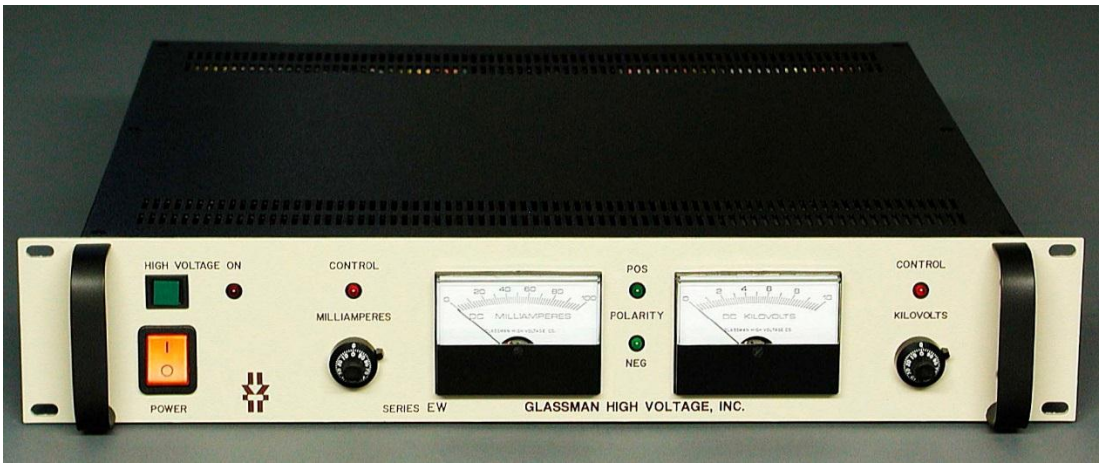

Figure 20: Glassman high voltage power supply [52]

7.1.1.2 Electrode Power Supply

Power has two primary components voltage and current. The temperature of an electric plasma is determined by the plasma current. The higher the current, the hotter the plasma will be. The ignition system can generate a cold plasma, but the temperature generated by this is not even close to those required for this reaction. The ignition system is responsible for producing the initial ions, once these are formed the breakdown voltage of the carrier gas drops significantly and allowing the low voltage high current electrode power supply to kick in and continue the plasma generation.

The power supply used is three 3 kVA AC-225 Lincoln Electric welder machines from Canadian Tire. These arc welders are designed to deliver between 40-225 A of current by adjusting the reactance on the secondary side of the transformer. They are designed to run on a single phase with an input voltage of 220 V.

A welder generally has a hot/working electrode which is attached to the stick and a cold/ground electrode attached to the workpiece. The reactor requires three working

electrodes with no ground and each electrode on a different phase so that at a given point of time there is always a potential difference across the electrodes thereby allowing arcing. This was achieved by rewiring the phases at the wall which were used as input to the welders. Each welder was supplied using 2 phases of the 3 phase source, (110 V line to neutral) wall supply as shown Figure 23: Wiring diagram for wall receptacle. It is important to note that the receptacles are wired as shown such that it creates a delta connection when the power supplies are connected to the receptacle, and the hot side is used in the reactor.

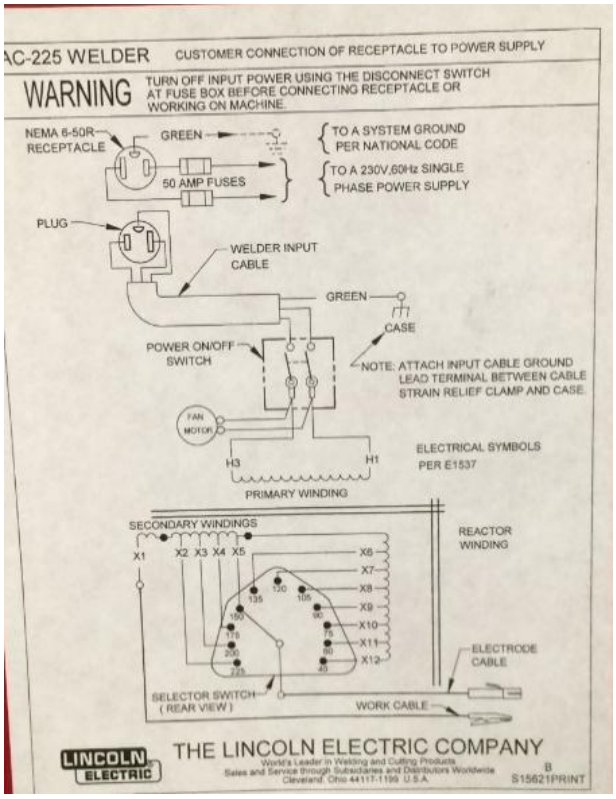

Figure 21: Lincoln electric AC-225 [53]

Figure 22: AC 225 internal electrical diagram [51]

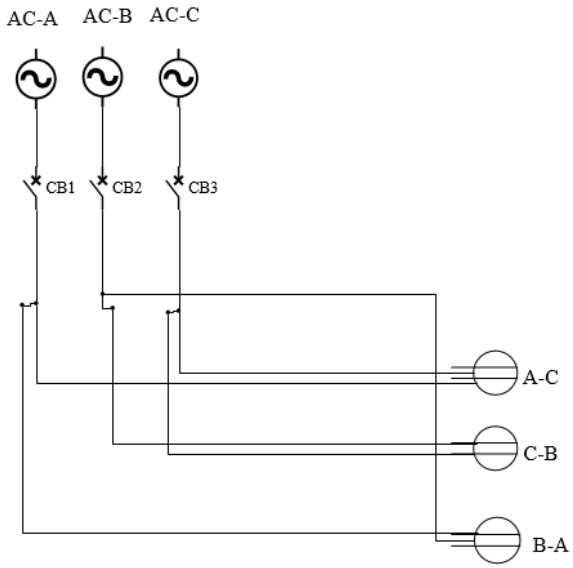

Figure 23: Wiring diagram for wall receptacle

7.1.2 Gas handling

Fullerene production requires an inert atmosphere. Nitrogen, argon, and helium are the three gases that will be used in the system. To control the flow rates of the gas going in three mass flow controllers by MKS systems were used along with CCR 400 controller. This was calibrated to measure flow at 25°C and ranged from 0-50 slpm for Nitrogen with an accuracy of ±.2% up to 10 slpm and ±1% between 10-50 slpm.

Figure 24: CCR 400 [54]

Figure 25: GE50A Flow controller [55]

7.1.3 Carbon injection

Solid carbon is the main feedstock for fullerene production in this reactor. Various grades of carbon black are expected to be tested as feed in the form of an aerosol. This is done using PFR400 by TEKNA plasma systems. This nano powder feeder can feed a vast range of particle sizes ranging from 10 nm to 5 µm (depending on an internal screening mesh used). It consists of a 12 litre hopper for the carbon with a wire brush attached to a

motor on a steel mesh. The rpm of the motor can be controlled between 0.0 and 40.0 thereby allowing precise control of carbon feed rates. Once the carbon falls through the mesh it is picked up by the carrier gas and a sonicator is used to ensure that the particles are properly suspended in the gas and do not aggregate. This aerosol is then carried over as feed to the reactor. The MOC for the powder feeder is highly polished SS and is equipped with various pressure gauges, a pressure relief valve and a heating tape to ensure dryness of the feed.

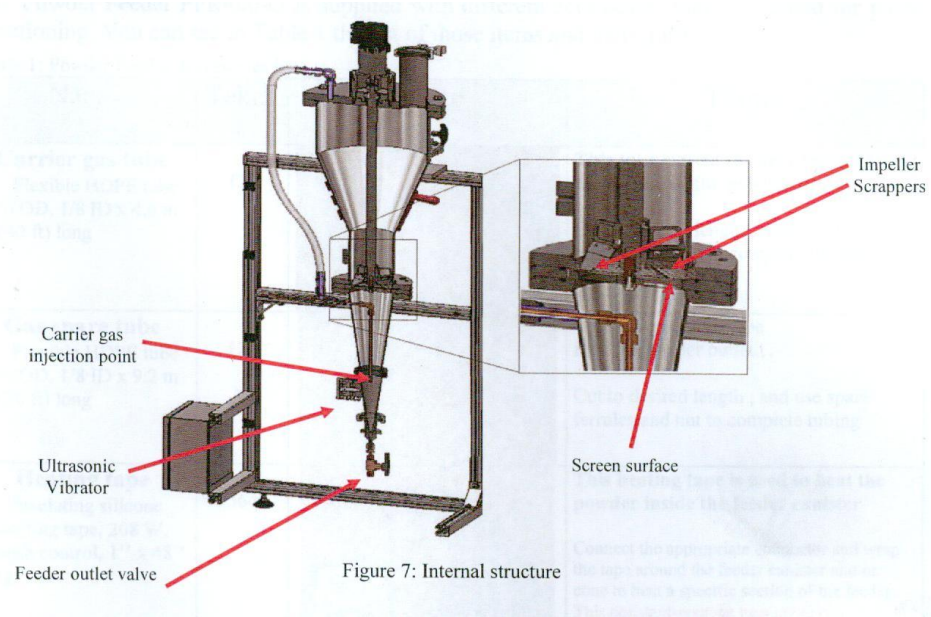

Figure 26: Tekna PFR400 nanopowder feeder [56]

7.1.4 Plasma torch

The Plasma torch is located at the top of the reactor. It consists of three water-cooled brass electrodes 120° apart which are encased in a graphite shell which in turn is inside a schedule 40, 8-inch tube. The electrodes are electrically isolated from the chamber using MACOR feeders as shown in Figure 27: MARK 1 plasma torch (all dimensions in the figure are in mm).

The graphite shell is thermally insulated from the steel using fiberglass wool and castable ceramic (Kast-o-lite from Thermal Refractories INC) to limit the amount of heat to the surrounding.

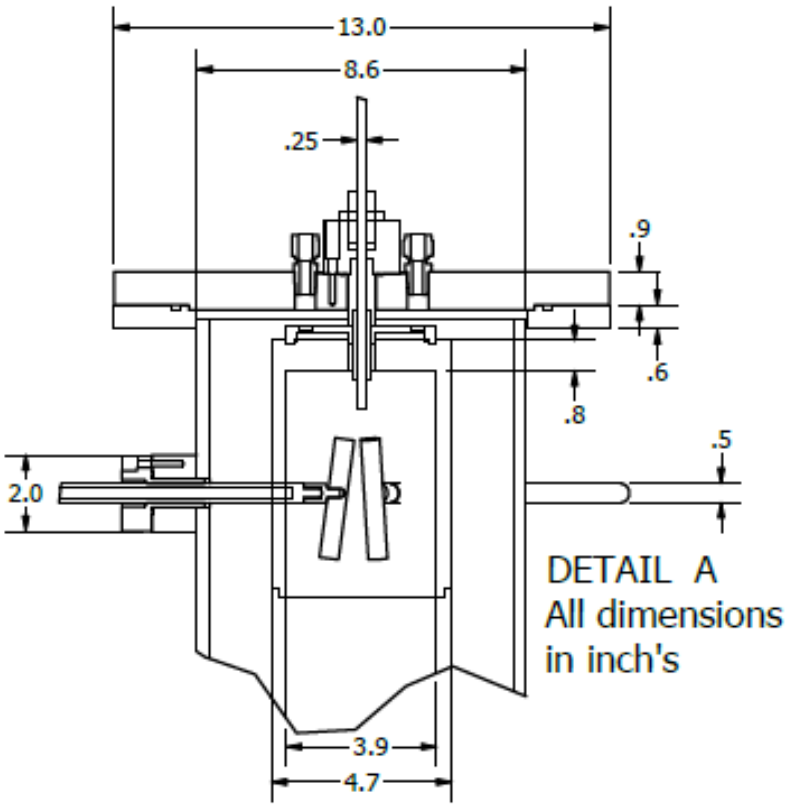

Figure 27: MARK 1 plasma torch

7.1.4.1 Electrode design and orientation

Jacobs ladder is a device used to produce continuous arcs which rise upwards. It consists of two wires which are vertical and form a narrow v but are not connected. These are then connected to a high voltage source and arcs are generated at the very bottom of the v where the gap is the smallest and they rise until the arc becomes so long that it loses stability and extinguishes after which another arc is generated at the bottom, and the cycle

continues. This effect mainly occurs because of the heated ionized air rises carrying the current path with it until the spark cannot sustain itself, keeping this in mind a diverging electrode was designed such that they diverge at a 15-degree angle with the center axis. The gas in the reactor is injected at the top and exits at the bottom, and it is expected that with sufficient gas flow the heated ions will travel along with the gas thereby propagating the arc along the electrodes.

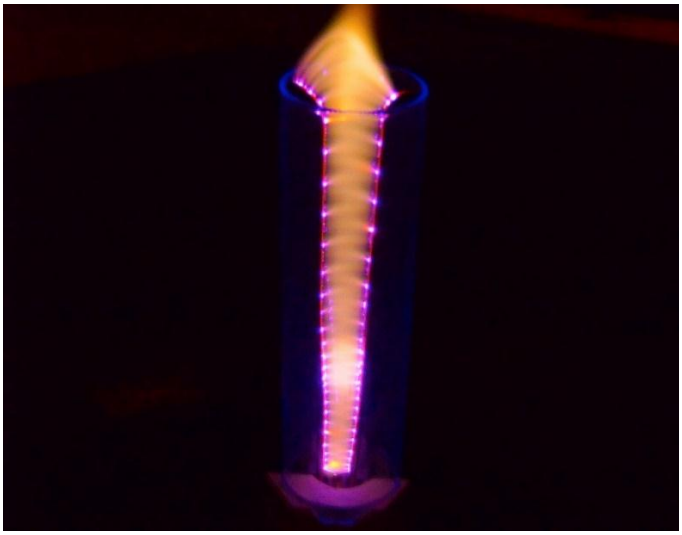

Figure 28: Jacobs ladder [57]

7.1.4.2 Carbon and Gas Injection

The carbon-laden plasma gas is fed to the center of the reactor using an injection probe. A sheathing gas is injected from two ports on the top into a gas reservoir through a ceramic disc. The reservoir ensures even distribution of the gas to the 6 injection lines in the graphite which are at 45 degrees to the central axis creating a vortex effect. This gas is primarily meant to protect the walls of the graphite chamber and to limit the plasma. The vortex is also expected to increase collisions between carbon ions thereby increase in yield.

7.1.5 Reaction zone

The zone follows the plasma torch, once the plasma is formed it tends to expand thereby reducing plasma enthalpy and might limit the evaporation of carbon. A converging region is placed after the torch to limit this thereby maximizing evaporation of the carbon. The converged shell is then kept at the same diameter for a short distance before it diverges back to the original diameter. This constricted region is called the throat is the main reaction zone. Here the carbon vapor is converted to fullerenes. The placement and length of the throat can be modulated. The gas flow rate and length and placement of these zones would affect residence times and evaporation rates.

7.1.6 Quenching zone

Once the reaction is complete, and the desired particle size is achieved the reaction needs to be quenched this is done by diverging the throat back to the original diameter thereby inducing cooling by allowing the gas to expand. The walls in this section are relatively cooler thereby allowing natural convective cooling. A quenching gas is also injected to aid cooling.

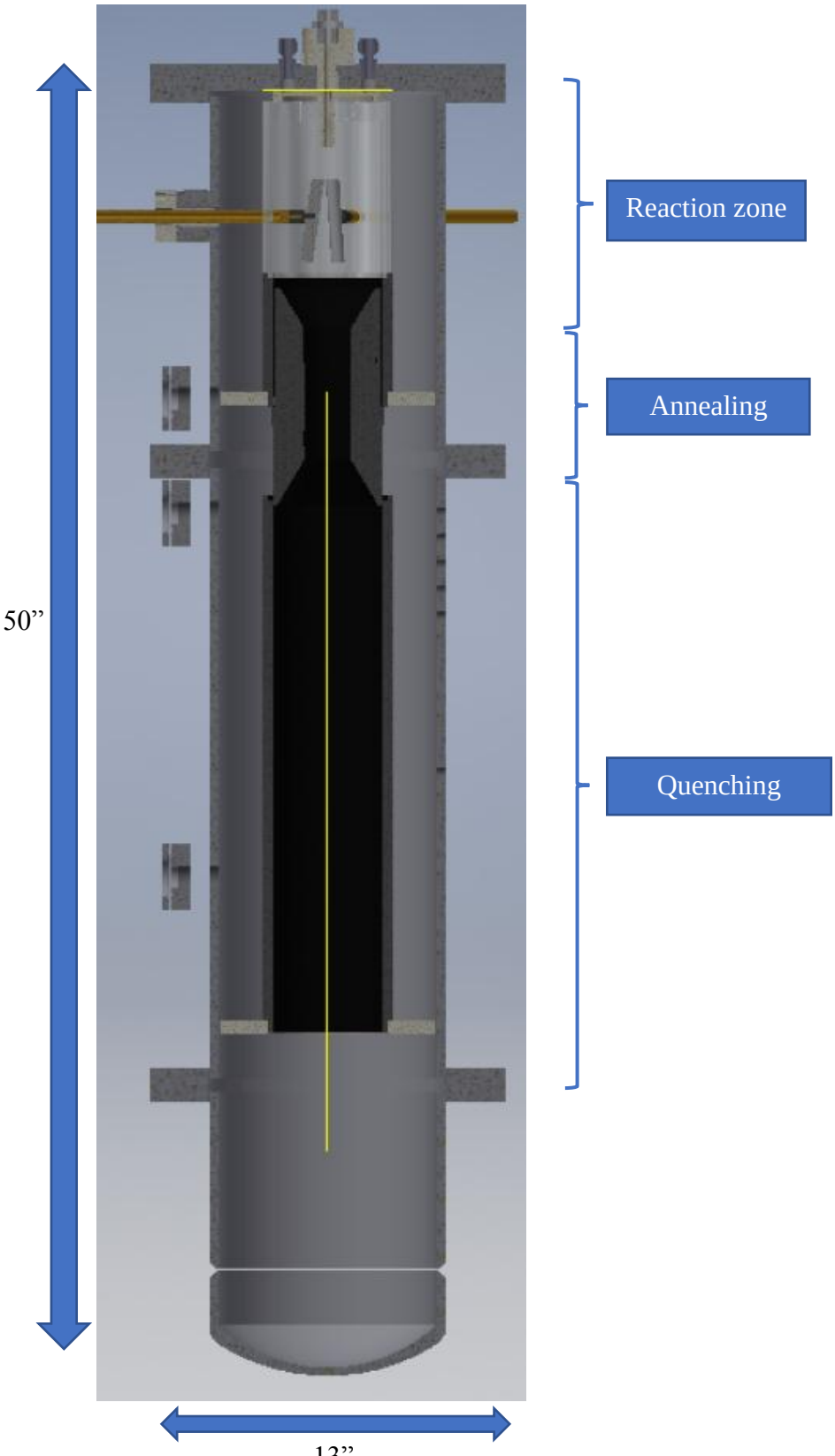

Figure 29: Mark I zones

7.1.7 Evaluation and discussion

Multiple tests to determine plasma stability and power supply limitations were conducted prior to starting the reactor to gain insight into plasma behavior. It was determined that at a higher current the plasma was more violent and seemed to be the hottest also once ignited it was easier to increase the distance between the electrodes at high currents.

Preliminary tests on the reactor provided an optimal range for gas between 8-20 slpm for helium as plasma gas when using tire grade carbon black (N660) as feedstock and between 15-30 slpm when using acetylene black as feedstock to maintain a stable plasma. The reactor was tested at various reaction conditions by varying currents between 40-225 A with both feedstocks at different flow rates and neck positions. No fullerenes were detected at any condition while using N660 as feedstock however at a max current of 225 A with a smaller particle size carbon black (N234) trace quantities of fullerenes were detected to provide us a qualitative result with an HPLC (Figure 31: Representative HPLC from Mark I).

Images of the soot samples were obtained using a TEM (Figure 30: TEM of N234 before and after Mark I) and a change in particle size and structure was detected in both grades of carbon and a presence of onion-like carbons was detected, this suggests that the plasma was able to evaporate both carbons however the impurities in N234 reacted with the carbon vapor before they had a chance to form fullerenes [51].

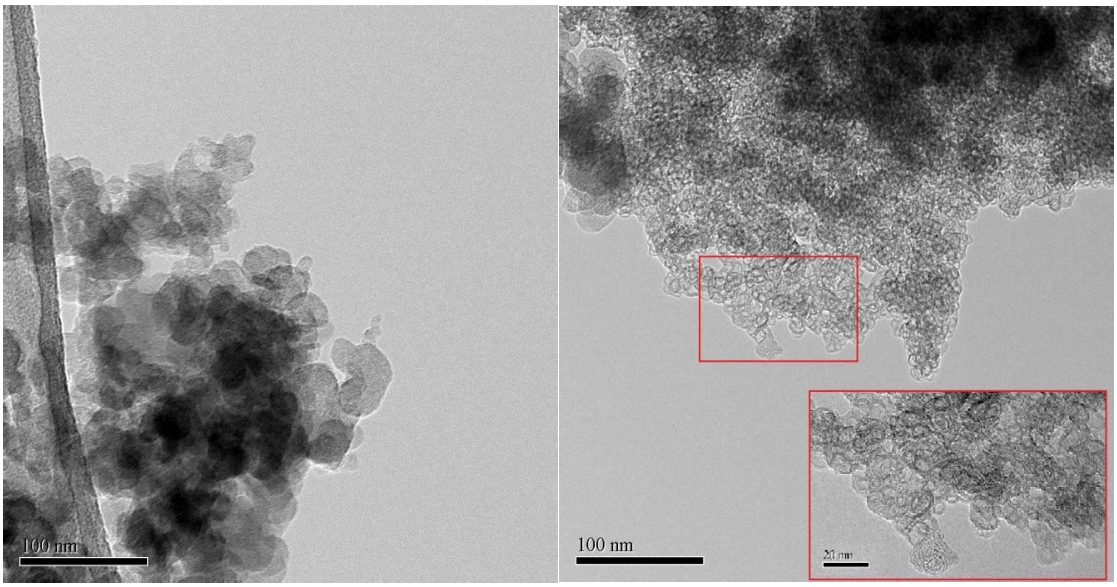

Figure 30: TEM of N234 before and after Mark I

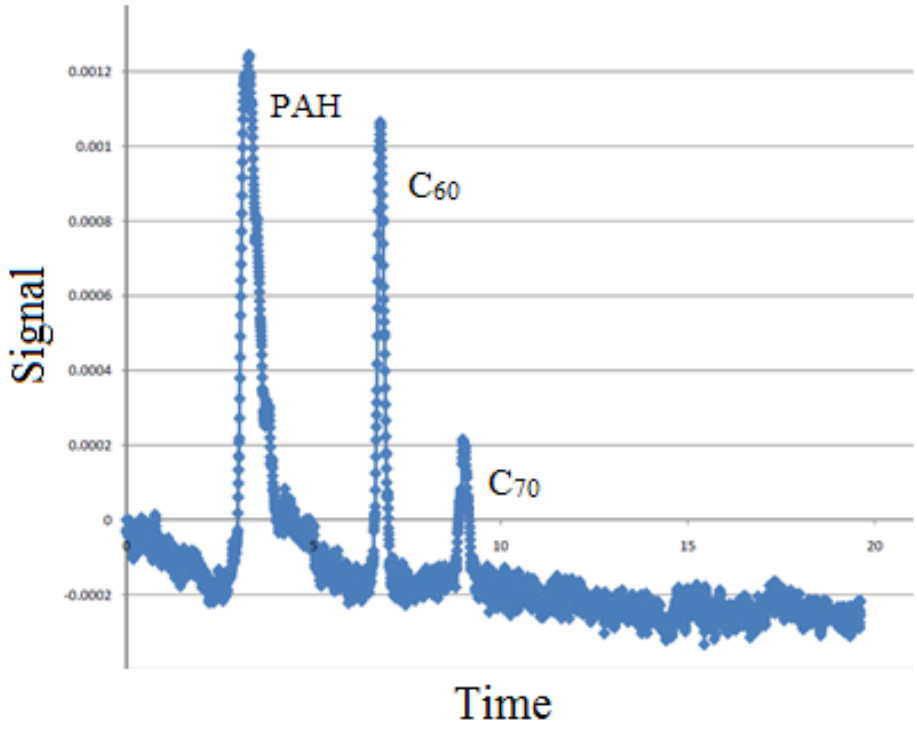

Figure 31: Representative HPLC from Mark I [51]

Testing provided insight into the design changes required to achieve a quantitative yield of 2% at atmospheric pressure. The upside-down Jacobs ladder did not work (because the gas flowrates being used were relatively low to counter natural convection), and the plasma was concentrated at the top of the electrodes where the distance between them was shortest, this led to overheating of the top flange which needed to be cooled and became a heat sink(as energy needed to be removed to keep the flange from overheating).

The vortex seemed to provide the desired effect in MHD modeling of the torch region without considering the carbon particulates done by Dr. Andrew Gerber's group from Mechanical Engineering @ UNB,however when tested in practice the particulates seemed to enter the sheath gas and bypassed the plasma entirely resulting in limited evaporation. The vortex was able to contain the plasma and would be ideal if one were to use the torch as a heat source; however, for the current application vortex seemed to be more detrimental.

The electrodes coming in axially also proved to be a challenge as the reactor needed to be taken apart to replace the electrodes which were impractical. Opening of the reactor also leads to other atmospheric impurities entering the system which needed to be purged prior to runs. Mark 1 was a good starting point and provided the team with invaluable experience with plasmas to make changes and design MARK II.

7.2 Mark II

Mark I was instrumental in providing necessary insight and experience with plasmas. Using this experience Mark II called for a complete redesign of the reactor. The power supply, gas handling, and carbon injection systems were kept the same as they did not seem to be a direct limitation. The plasma torch was redesigned and moved from the top to the bottom of the reactor, thus allowing the plume to rise naturally in oppose to countering the convection currents like Mark I.

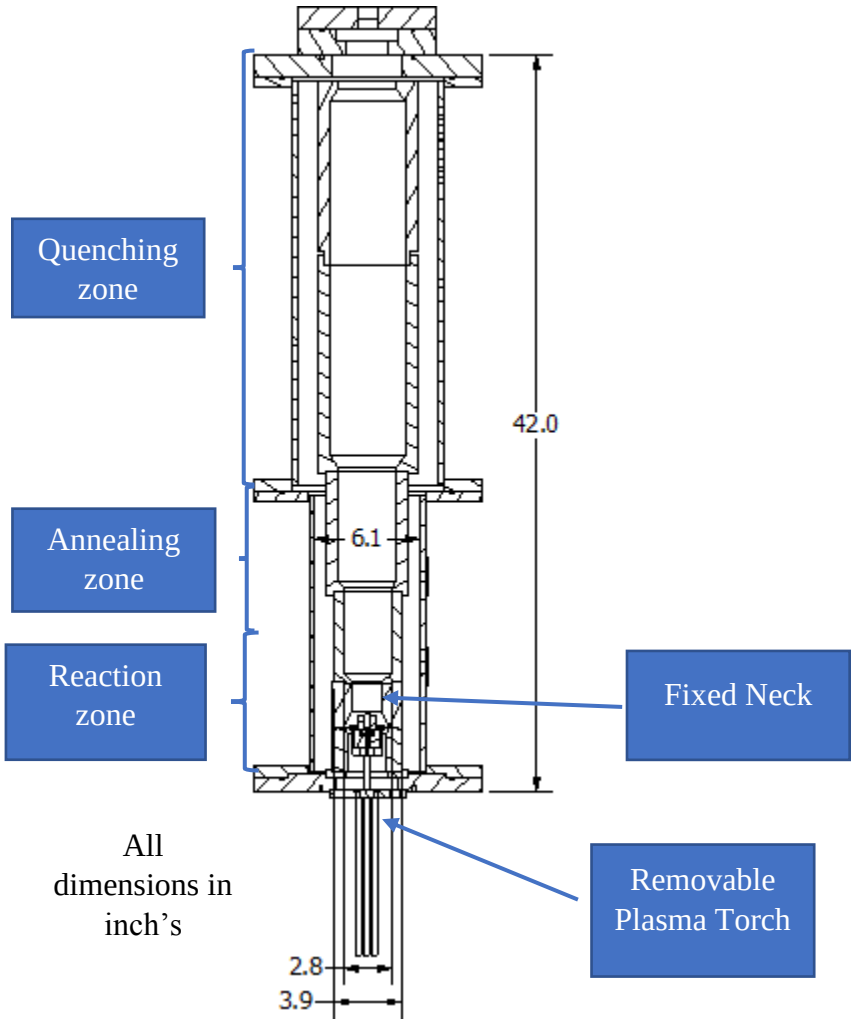

Figure 32: Mark II

7.2.1 Reactor design

The electrodes now enter the system from the bottom of the reactor. They are still 120^0 apart, but since the torch can be removed without having to dismantle the entire reactor, it makes it more practical. The Jacobs ladder was discarded, and a new design with three electrodes in the shape of a pie is tested. There is a boron nitride spacer (good electrical and thermal insulator) in between to electrically isolate the three electrodes. The sheath gas was eliminated, and the carbon-laden gas enters the reactor through two holes at the bottom from where they are directed into the plume at an angle. The idea of a movable neck was also switched to a fixed neck.

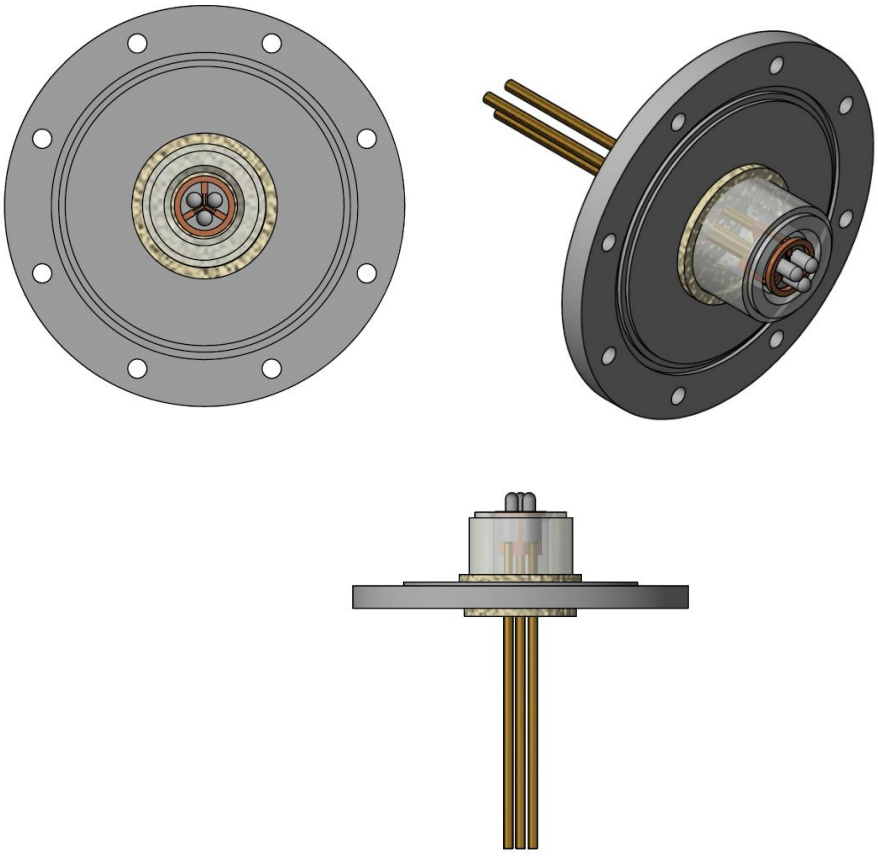

Figure 33: Mark II Torch top and side view

Figure 33: Mark II Torch top and side view shows the electrode assembly in the reactor the brown depicts boron nitride spacers.

Thermocouples were introduced at various distances across the reactor to record temperature profiles. A basic LabVIEW data acquisition system was developed with the idea of integrating the system further with the control as development progresses. Three oscilloscopes were also connected to monitor current and voltages of the power supplied to the electrodes.

A heating tape was wrapped around the inside of the top shell to reduce preheating times to ensure the reactor is hot enough for running. The heating tape also makes the purging process easier and quicker.

Two interchangeable setups for the collection were designed:

a) the soot-laden gas would leave the reactor from the top which would then be collected upon exit (Figure 32: Mark II)

b) a high temperature ceramic filter would be introduced at the top of the reactor, the fullerene vapor leaving the bottom chamber is hot and if the top chamber is maintained above 500°C then the vapor should be able to pass through the filter and then the purified fullerene could be either collected on a cooling finger or the fullerene laden gas can be cooled and filtered upon leaving the reactor. This allows the unreacted soot to fall back into the bottom chamber allowing it to evaporate and react (Figure 34: Mark II with filter)

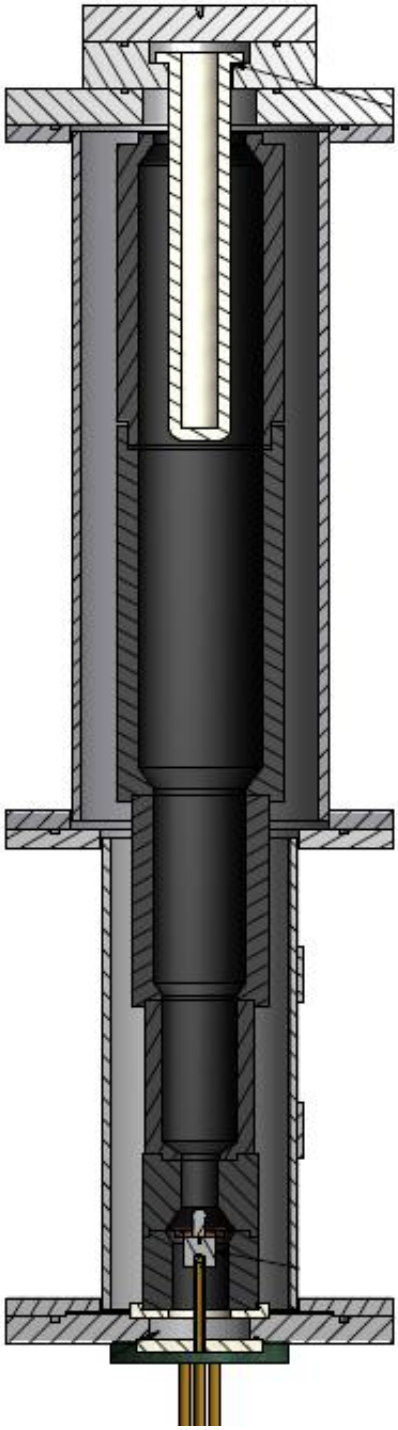

Figure 34: Mark II with filter

7.2.2 Evaluation and discussion

Mark II was a huge improvement over the previous design. The problem of excessive heating of the back flange was solved and is no longer a limiting factor on run time. The plasma quality was improved and entered the neck region. The removal of the sheath gas did not seem to affect the structural integrity of the graphite shell even after 100+ hours of running.

The carbon evaporation improved, and for the first-time measurable quantities of fullerenic soot was collected from inside the reactor. The fullerene content in the soot was under 0.5% which is extremely low. The installation of the heating tape was a good addition as it reduced the preheat times by half. Addition of LabVIEW and oscilloscopes helped understand plasma characteristics better.

The setup did not function as designed because the power supply started to overheat and could only give a run time of 2 mins at maximum current before needing shut down. The 100% duty cycle for the welders is only 125 A which is not enough for our experiments. The collection method with the filter in the reactor did not work because the unreacted soot would fall back into the plasma and with the new carbon being fed into the reactor it would extinguish the plasma. It was also determined offline that optimal purification conditions and plasma conditions were not similar and to run efficiently doing the separation offline was the best solution.

The pie electrodes did a good job at keeping the plasma stable however the assembly with the four boron nitride spacers was tedious also the pie design did not seem to provide any advantages and started to limit the plasma volume. It also served as an

obstruction to the carbon been fed. Four more configurations with the pie were tried, but none of them seemed to provide a stable large volume hot plasma.

The angular feed also seemed to get clogged often and was rather difficult to get the position of the electrodes just right to ensure that the carbon was directed into the plasma, most times the carbon would either hit the electrodes and fall down on the torch thereby creating a short between the electrodes on the macor thereby leading to localized heating on the torch leading to failure.

Macor is a good thermal and electrical insulator; however, its resistance to thermal shock under stress is limited. Multiple cracks were detected in the macor due to thermal stress.

Mark II was an order of magnitude better than the original design and quantifiable fullerene formation at atmospheric pressure was detected. Keeping all the design and power constraints in mind and after having tried multiple different configurations a complete redesign is in order.

7.3 MARK III

Mark II was a step forward to achieve our goal of 2% yield at atmospheric pressure. Multiple limitations were detected with respect to the electrode tips and power supply. This is addressed in Mark III.

7.3.1 Power supply

The Lincoln arc welders were good off the shelf solution to try for initial studies, but they started to become a limitation. Ideally, a variable inductor with a capacitor in parallel just as used in a 3-phase induction motor with a high-power factor would be perfect. It was determined that the power in the current location was insufficient. The lab needed to be moved to another location with more power, in the order of 600V 3 Phase,100 A on each phase. Once this was acquired a step-down transformer to go from 600 V to 220 V phase-phase in a delta connection was acquired and connected. A variable inductor to limit the current was the next piece needed to prevent runaway current, to do so three identical high-power single-phase transformers were acquired from an industrial partner. Since a transformer is simply two inductors, it was decided to use the secondary (high current) side of the transformer as an inductor while leaving the primary isolated (Figure 35: Electrical circuit diagram of the electrode power supply). The calculated inductance value for the required current was around 4.2 mH. Major losses were expected in terms of hysteresis and eddy currents since no capacitors were connected in parallel to increase the power factor large amounts of reactive power is expected. This would not be used in the ideal world; however, for the proof of concept, it was decided to go forward and test the

prototype. The system was accessed for safety by a licensed electrician. Smart fuses were installed on each line for safety in case there is a runaway current. A 00-gauge wire was used to make all connections. Multiple fans were also installed on the step-down transformers and the inductors to ensure enough cooling. This was also monitored using a thermal infrared camera to ensure safety.

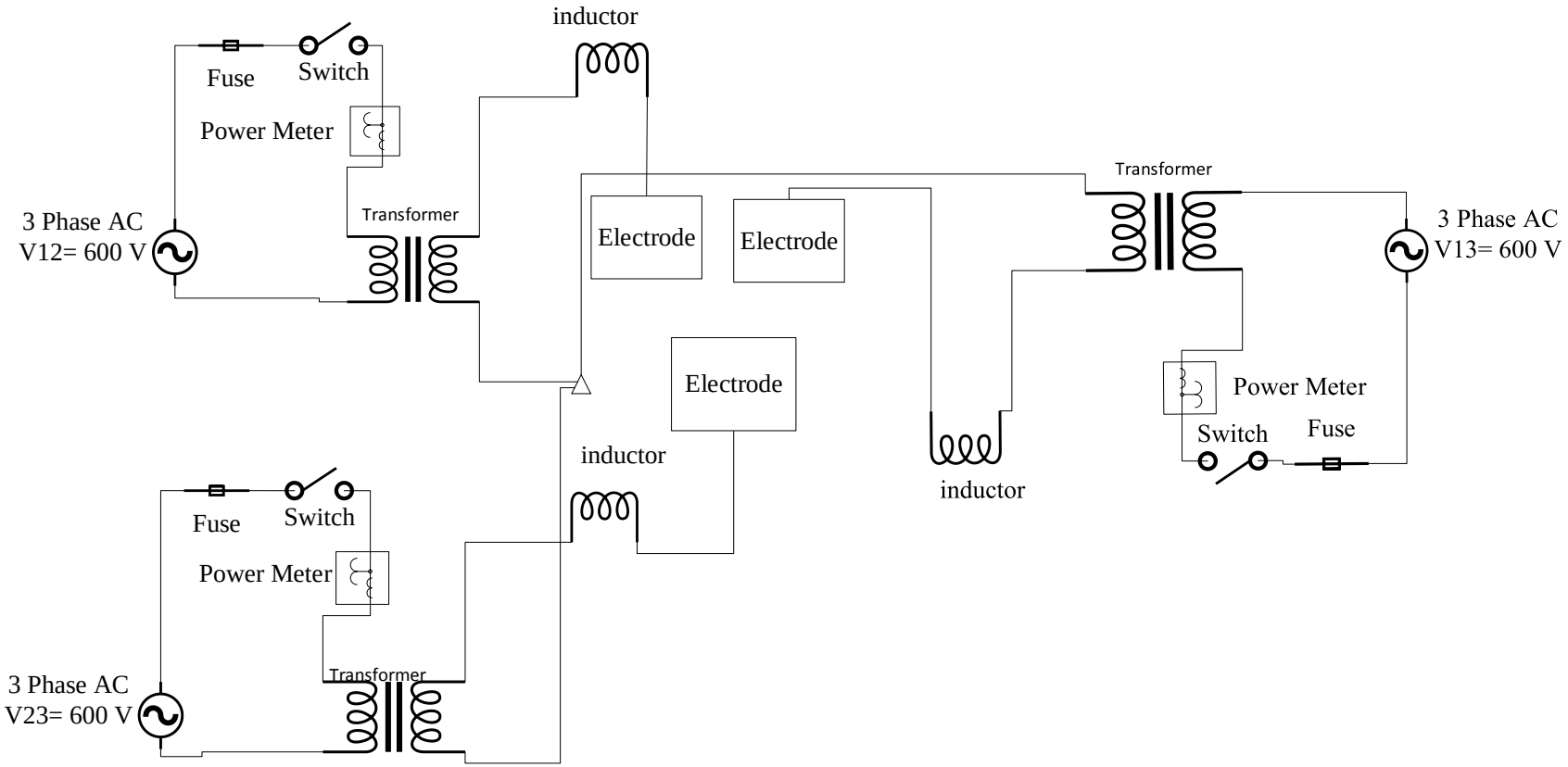

Figure 35: Electrical circuit diagram of the electrode power supply

7.3.2 Plasma torch

The Plasma torch in Mark II had multiple issues such as the alignment of the electrodes with the carbon feed ports, shorting of the electrodes on the main torch surface leading to failure of the MACOR, and the complex assembly of the pie with the boron nitride spacers which provided no added benefit and limited plasma volume to within the electrodes. These are fixed in Mark III. To start with MACOR is no longer used in the plasma torch, a replacement was needed. The new material needed to be an electrical and thermal insulator should be machinable and have high thermal shock resistance. Ideally, it should have a high operating temperature and a clean, sealable surface. After extensive research, the only material which fulfilled all our mandatory parameters was G-10, a high-pressure fiberglass laminate. It has high strength, is an excellent electrical and thermal insulator and has high thermal shock resistance. However, it has a low operating temperature of 138^0C, using it as a plasma torch material would be perfect if there was some way to ensure that the G-10 did not see temperature greater than 130^0C. To do so initial testing was done with the new electrode set up to determine the max temperature seen at the G-10 following which two insulators were chosen to protect the G-10 from the radiation from the torch. The first layer consisted of fire bricks used to line fireplaces which were machined to sit right above the G-10 this has a service temperature of around 140^0C and a thickness of 1”. The second insulator sits above the first, and just below the electrode tips this is a high-temperature castable ceramic and is good up to 2200^0C. The reason the castable ceramic is not used as the first layer is that it is extremely difficult to machine and with the tight clearances it was extremely difficult to make one without cracking it.

The carbon feed ports needed change as well, and it was necessary to simplify it and ensure that every run carbon was fed into the plasma and did not just go around or fall out from the aerosol. To do so, a direct injection from the center along with the plasma gas directly into the plasma was designed. The injection tube is made of G-10 to ensure electrical insulation, and this takes the ambiguity of electrode alignment away from the setup.

7.3.3 Cooling system

The cooling system for the electrode did not have any real issues on Mark II; however, a couple of changes were made to ensure all electrodes were getting equal cooling. To do so flow meters were installed on each line to maintain equal flows.

7.3.4 Reactor design and controls

The inside of the reactor was kept the same as Mark II; an extra insert was constructed to fit into the throat region to make It narrower and longer as it is suspected that there is insufficient time for the dimers and trimers to form fullerenes. The elongated and narrower throat should increase collisions and improve yields. This theory shall be tested by running the reactor with the original throat followed by the insert at same conditions.

The control system also needed some automation, to do so all the gas mass flow controllers are now controlled via an intranet system which was set up. A LabVIEW system was programmed to monitor temperature at various zones of the reactor (Figure 39), the

power delivered, pressure and gas flow flowrates as showing in figure 36-38. Figure 39 presents the temperature profile during a typical pre-heating cycle and run. Temperature 1 is measured at the outer graphite shell closest to the plasma, with each subsequent temperature further away towards collection.

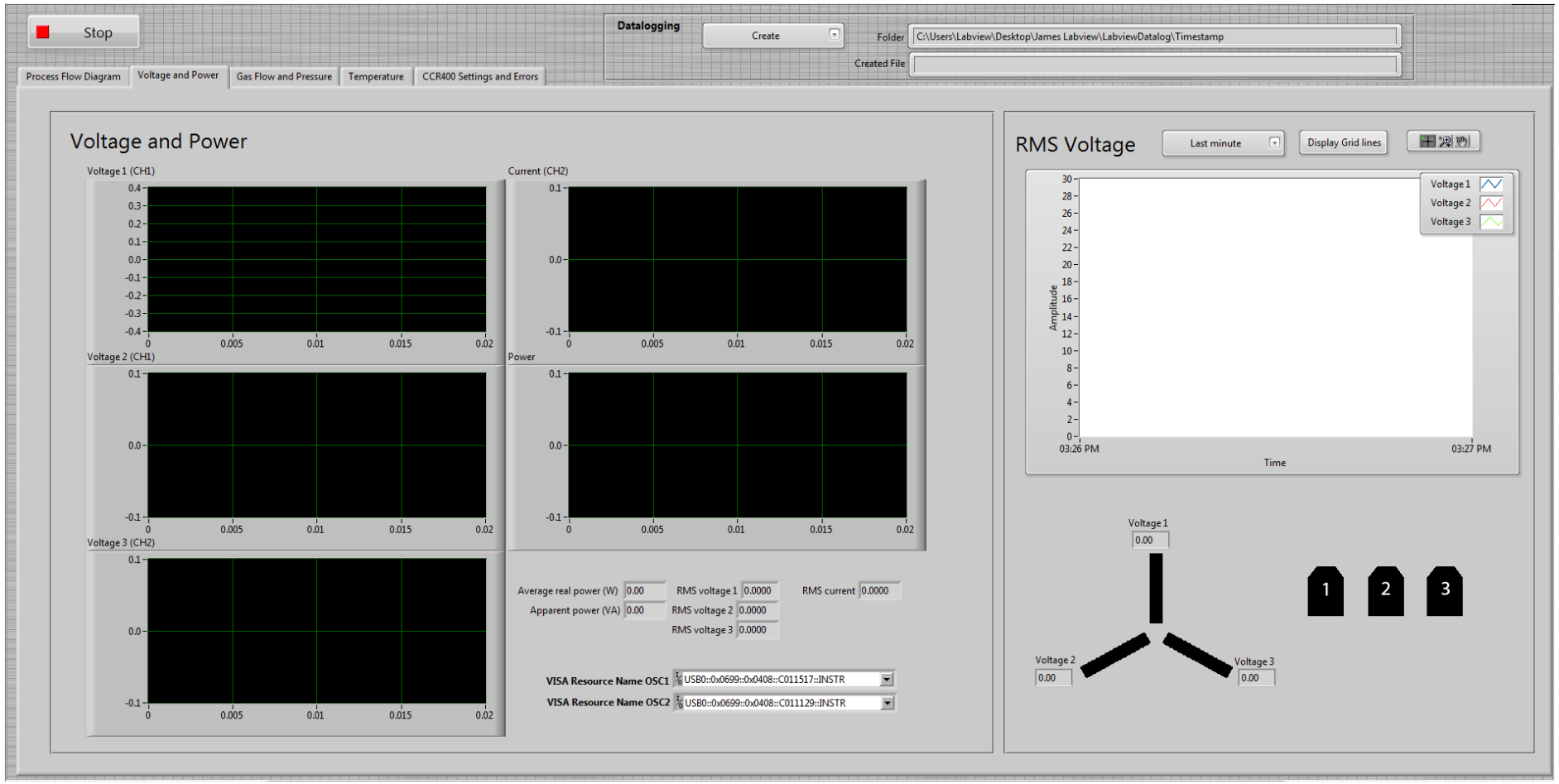

Figure 36: LabVIEW live power reading screen

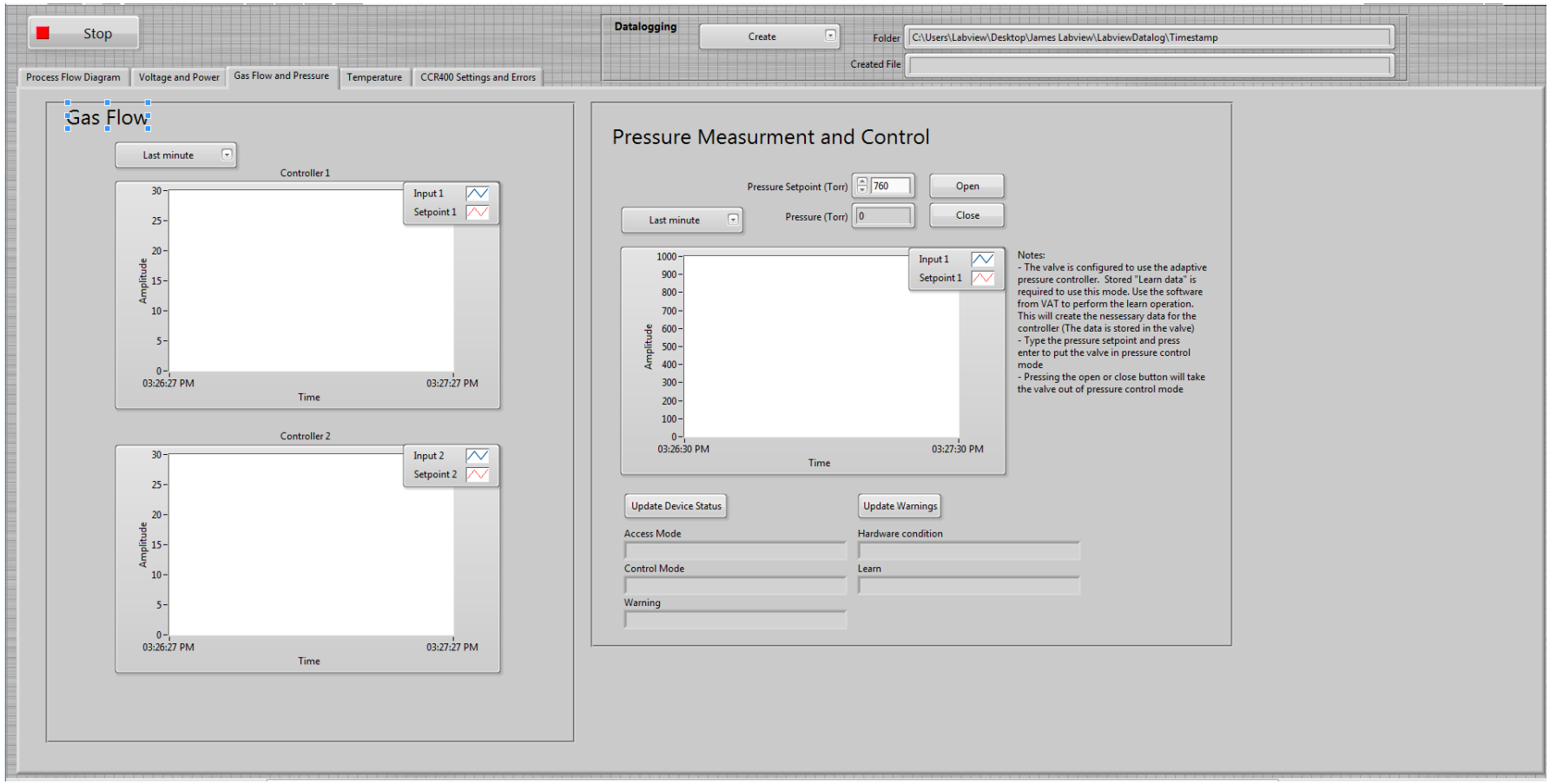

Figure 37: LabView pressure and gas monitoring

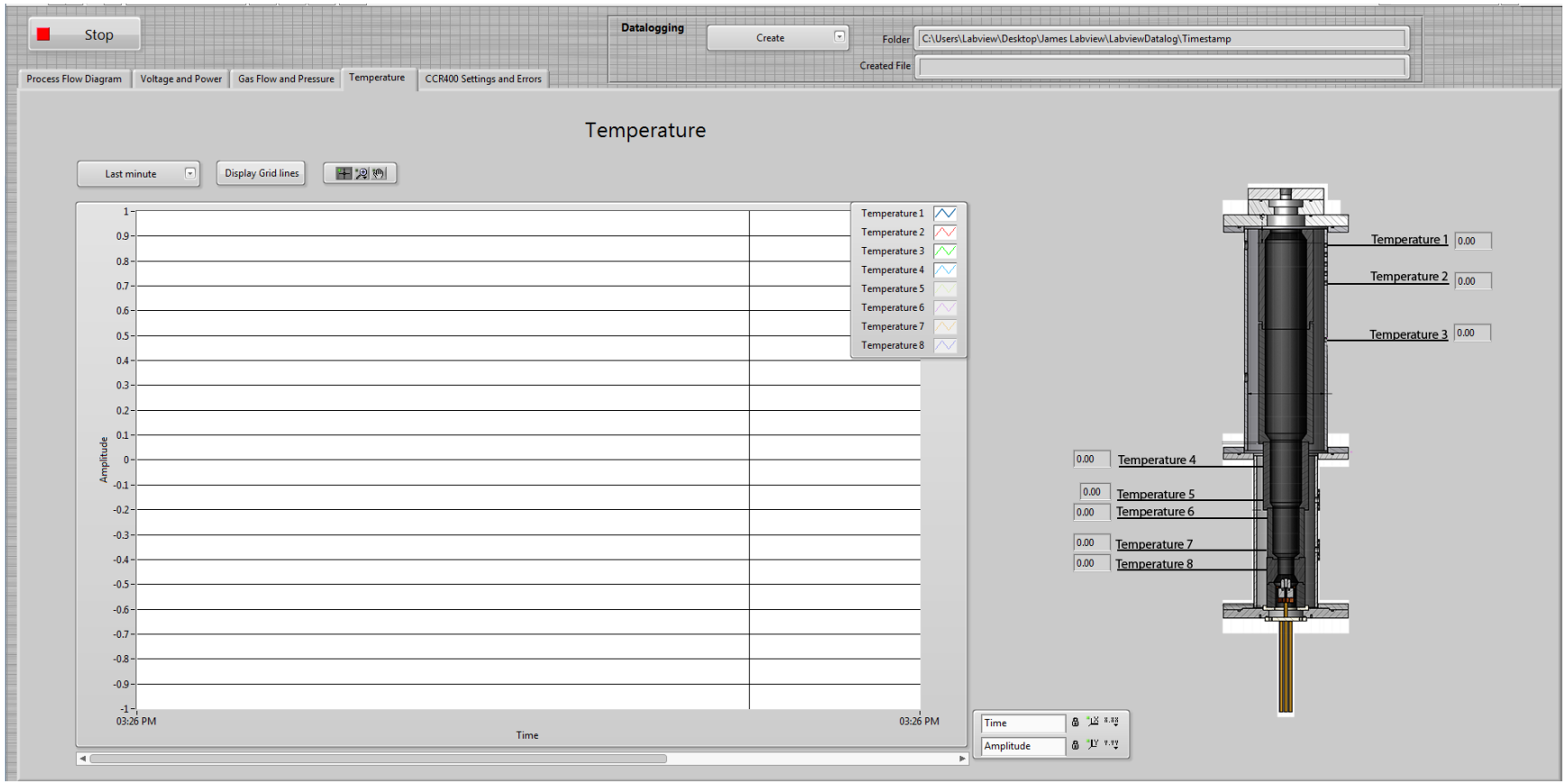

Figure 38: LabView temperature monitoring

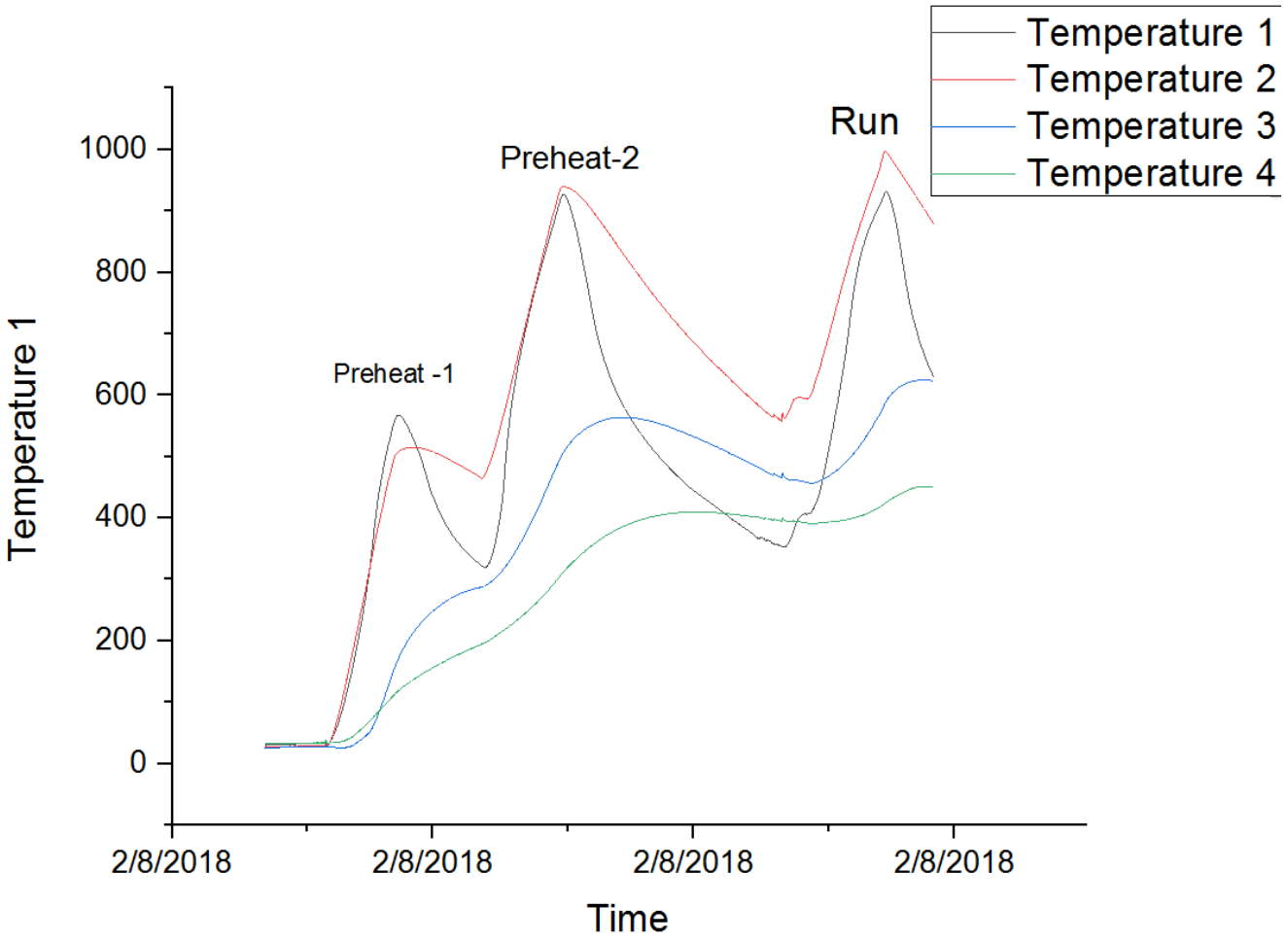

Figure 39: Sample temperature monitoring graph

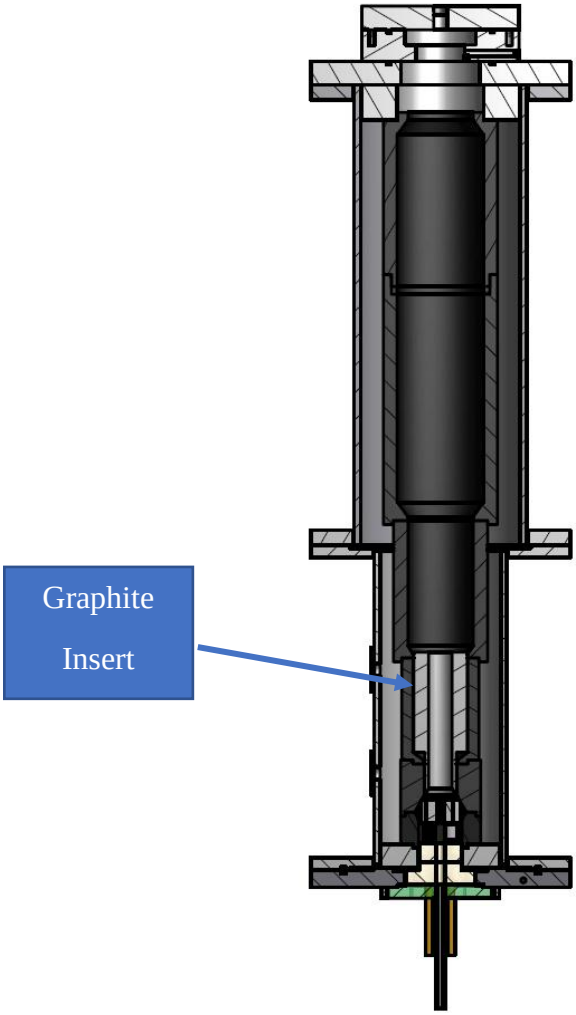

Figure 40: Mark III with insert

7.3.4.1 Electrode Tips

The pie electrodes from Mark II needed change as it was a complex assembly and was limiting the plasma volume. After multiple iterations of design and testing, a new design was implemented. The electrodes are still brass with graphite on top. The graphite section is now three parts, the first one being the adapter the second being the holder and

the third being a nub. The nub is threaded into the holder, and the holder is threaded into the adapter which in turn threads into the electrode.

Overall this set up seems to provide the largest volume stable plasma.

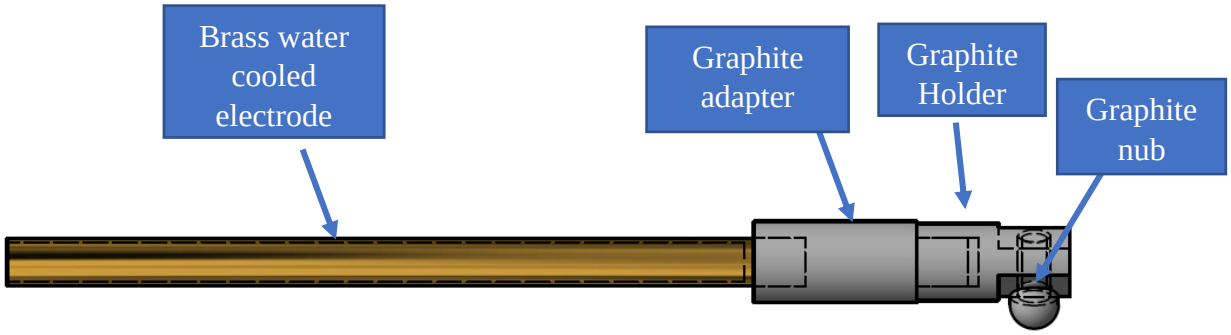

Figure 41: Electrode assembly MARK III

7.3.4.2 Nubs

The graphite nubs are consumable. They basically function as a fuse wire. The plasma starts between these nubs as they are close to each other the breakdown voltage is low, as the temperature increases the arc expands and moves to the tips of the holders. The nubs get consumed after a helium run and need replacement.

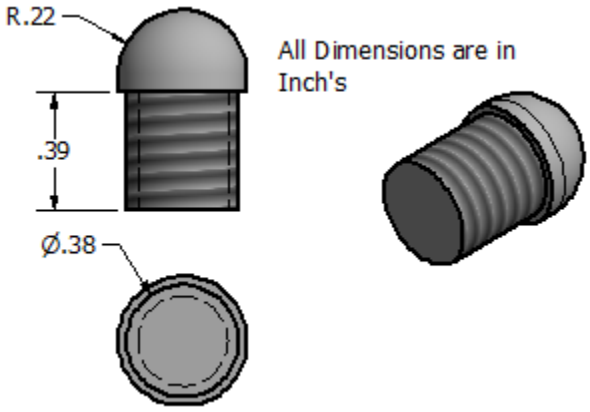

Figure 42: Electrode nubs

7.3.4.3 Holders

The holders are responsible for holding the nubs in place. The plasma arc eventually shifts on to the holders, and this results in a large volume plasma. The holders do erode and need replacement about every 50 hours.

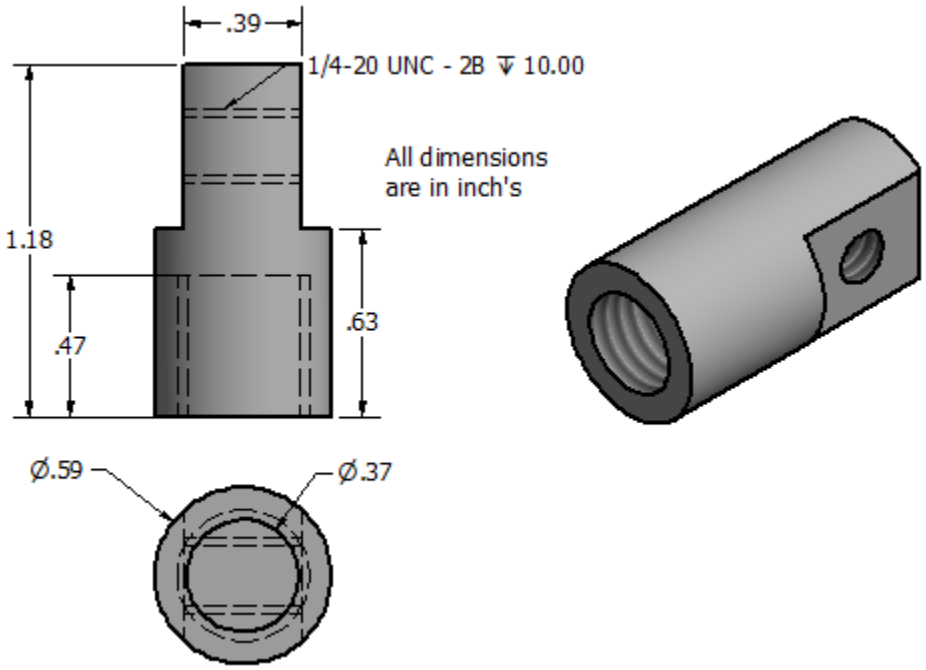

Figure 43: Electrode holders

7.3.4.4 Adapters

The graphite adapters simply serve as a transition zone to create a temperature gradient between the holder and the brass electrode. On connecting the holder directly to the electrode, the gradient was insufficient and lead to melting of brass threads over time. One could increase the length of the holder itself, but as holder do require replacement, it would be a waste of material as adapters need no replacement.

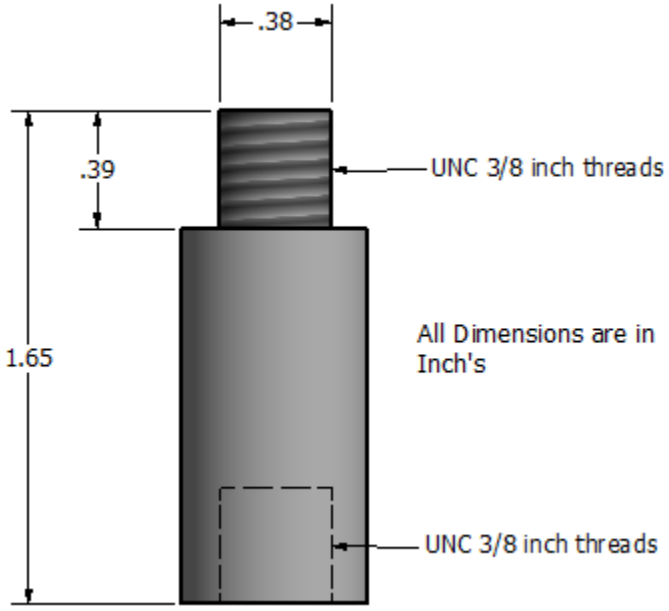

Figure 44: Electrode adapters

7.3.5 Evaluation and discussion

Mark III was a success. Fullerene yields as high as 3.5 % at atmospheric conditions while using the insert were obtained. Without the insert, the max yield obtained was about 1%. The new plasma torch did not have any issues with heating and the max temperature recorded was about 80^0C. The carbon was entering the plasma and was not dependent on the electrode alignment. The new power supply also allows runs up to 20 mins in helium, it does tend to heat up after that possibly because of the large amounts of reactive power going through the system. The bottom flange requires no cooling as the max temperature recorded was only 60^0C.

The 3% yield with the insert also helped us conclude that the venturi effect created in the reactor impeded fullerene formation and if a design change was made it could lead to higher yields. To possibly check sub-atmospheric runs a leak test on the reactor was conducted and multiple leaks were detected at the welds and NPT fittings. It was also determined that the feeder was only meant to operate at atmospheric pressure. With the atmospheric pressure yield objective being complete two other tests wereconducted on the system:

A) Determination of recyclability of helium and the effect of impurities on fullerene yields which was a part of Jun Ha Lee's thesis, it was established that a gas purity had a major effect on yield. To achieve an acceptable yield a minimum gas purity of 99.8 vol% is required.

B) The other study was done by changing to another feedstock namely N234 which is a cheaper carbon with more impurities to produce onion like carbons as presented in a

group members master's thesis. It was determined that increased carbon impurity lead to no fullerene formation. It was however successful in forming OLCS.

These two experiments along with our previous experiments and experience resulted in another redesign to see if we can further improve these yields at atmospheric conditions.

7.4 MARK IV

MARK III achieved our initial objective of 2% yield at atmospheric pressure, and sub-atmospheric runs were not possible due to leaks and the powder feeder. The increase in yield with the increase in collisions and the results from the two other studies provided us enough confidence to build another generation which would improve the yield further at atmospheric pressure, and it was time to test the same. Multiple changes were made to the reactor itself along with additions of various instruments for diagnostics while keeping the rest of the set up the same as Mark III.

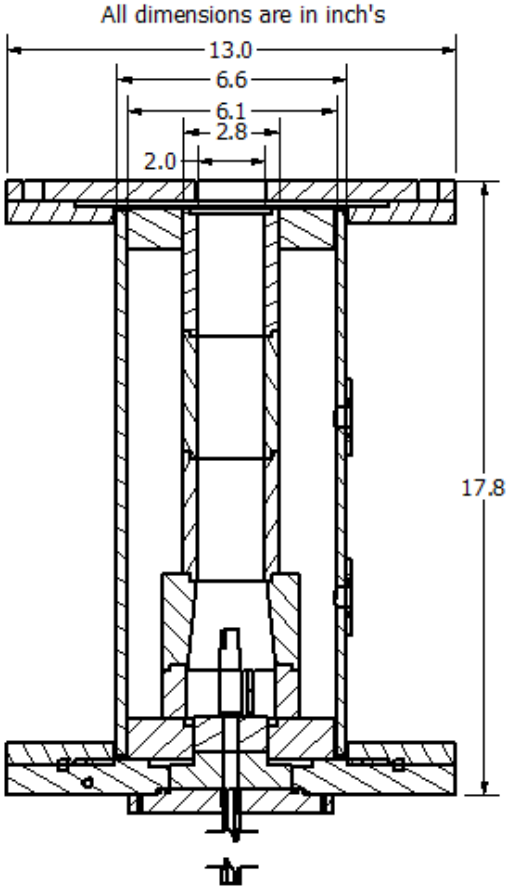

Figure 45: Mark IV

7.4.1 Reactor design

7.4.1.1 Steel shell

The flanges on the steel shell were welded from the inside to ensure proper sealing. It was also determined that the bosses on the reactor were only welded from the outside and had virtual leaks on the inside. This was rectified by welding them on the inside. All the NPT fitting were leaking even though they were tightened with Teflon tape, to limit the leaks the fittings were welded to the shell from the inside. The top chamber of the reactor was discarded.

Additional gas connections were made at the windows to provide positive pressure and limit inflection of air. An additional adapter was constructed to introduce a potassium bromide (KBr) window for IR Spectroscopy.

7.4.1.2 Graphite shell

The graphite shell of the reactor was modified to go from 66 mm at the electrodes to gradually transition to the throat which is 55 mm in diameter. This throat region now continues till the end of the reactor where it exits into the collections system. The modification to the initial section was made as in Mark III it was determined that the expansion zone for the plasma was responsible for limiting carbon evaporation as it lowered plasma density and provided more space for the carbon to bypass through.

7.4.1.3 Collection

Once the gas exits the graphite shell, it enters a steel tube at the same 2-inch diameter which then tangentially transitions into a bag house where the soot is collected, and the gas exits the system.

7.4.2 Instrumentation

7.4.2.1 Temperature monitoring

The temperature in the reactor is ever changing with the plasma; it is extremely important to monitor the temperature throughout the reactor for any spikes in temperature which may lead to localized failures. Various thermocouples are installed on the reactor which are then connected to a data acquisition board, and the readings are recorded using LabVIEW. The error of the thermocouples along with the fact that the thermocouple is a source of indirect measurement may provide readings within a ±50℃ which is acceptable as it is solely used for failure monitoring and has no direct role in the operation of the system.

7.4.2.2 IR Spectroscopy

Figure 46: iHr 320 IR spectrometer [58]

Fullerenes (C_{60}, C_{70}, C_{84} and so on) have been detected in space by observation of the absorption of infrared radiation using powerful IR spectrophotometers. C_{60} is highly symmetric, and for such a large molecule, only has 4 IR absorption bands, due to this symmetry. These absorptions are found at IR wavelengths of 7.0 μm, 8.5μm, 17.4 μm, and 18.9μm. This is a useful feature that allows C_{60} to be detected in the gas phase. The absorption at 18.9um is best to use because many PAH species interfere with the other three absorption bands. In this way, the presence of C_{60} was monitored in real-time using iHR 320 Infrared Spectrometer by Horiba Instruments was used and calibrated for different vapor pressures. (this information can be found in detail in Eric Fradsham's Thesis [59].)

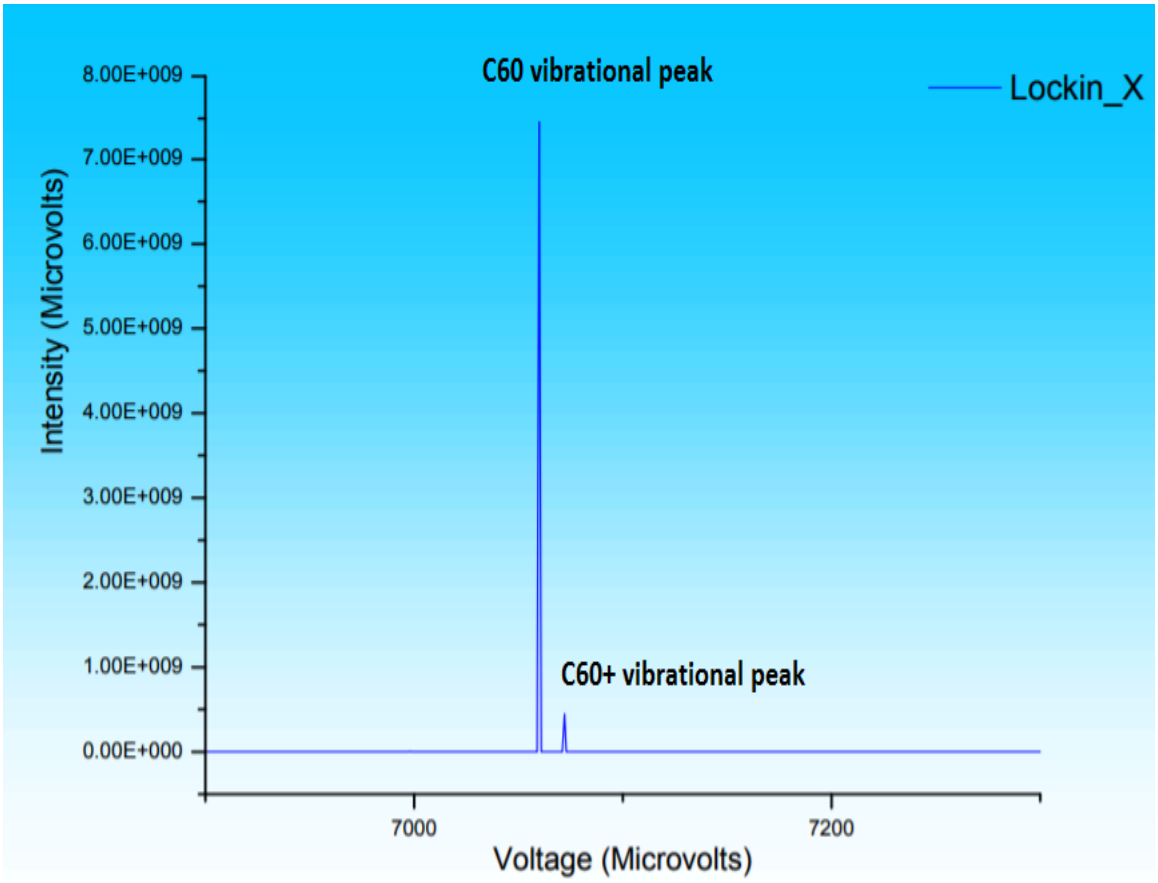

Figure 47: Sample IR spectrum for C_{60}

7.4.2.3 Optical emission spectroscopy

Figure 48: iHr 550 OES [58]

When carbon evaporates it produces carbon vapor which reacts to form C2, C3 dimers and trimers, these radicals emit green light in the range of 425 nm -625 nm called swan bands. These are measured using an optical emission spectrometer. Emission intensities alone provide limited insight into fundamental plasma parameters. Because the emission intensity depends strongly upon both excitation and non-radiative deexcitation rates as well as radiative decay rates, it usually does not provide information on the ground state species concentration [60]. In Mark IV the electric arc used to generate the plasma is the excitation source, this is not constant and varies at a frequency of 60 Hz this limits us in forming a direct relationship between emission intensity and yield. Furthermore, this

emission is measured along a line of sight, which limits detection of localized variations, solid carbon may also be in the line of sight which may reduce the intensity. The graphite chamber also heats up emitting light which interferes with the baseline. IHR 550 from Horiba Instruments was used to detect C2-C3 formation in the reactor, the presence of impurities and to provide some insight into the plasma characteristics. (the results and detailed information can be found in Eric Fradsham's thesis [59].)

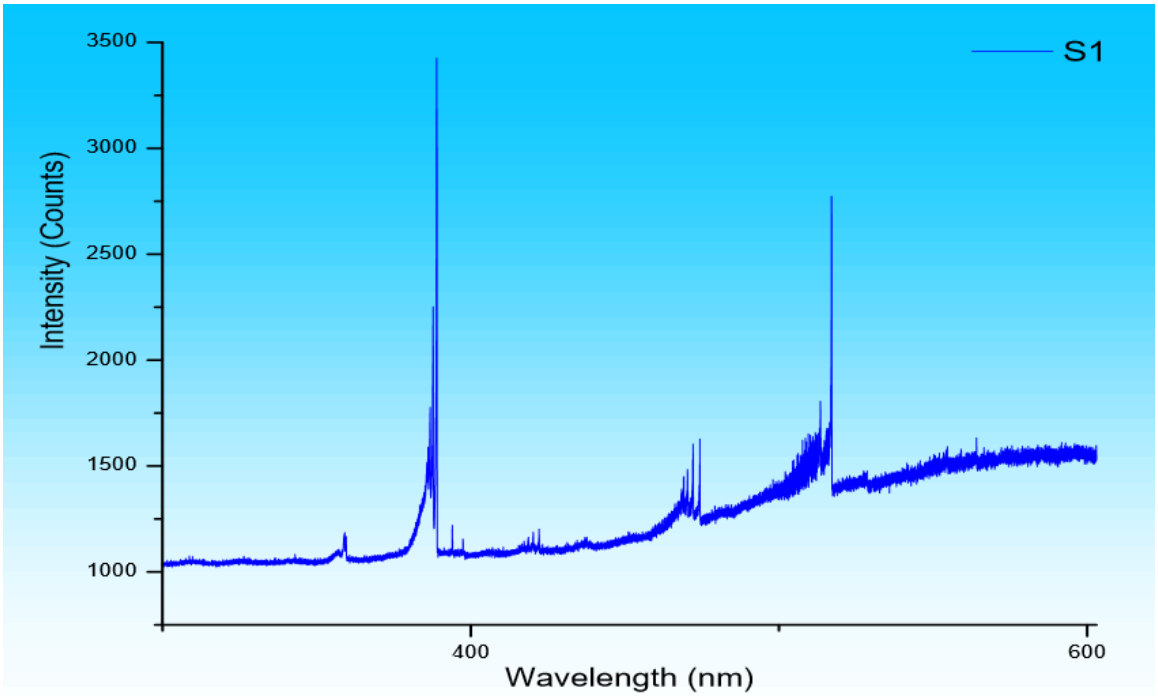

Figure 49: Sample graph from OES

The sample graph in Figure 49 [59]shows the presence of CN radicals at 389nm, C2 at 474nm and 517nm prior to feeding carbon in an argon plasma. The intensities are arbitrary and can be used in the relative sense to obtain a relationship.

7.4.2.4 Power Analysis

A power meter was installed at the wall to determine the power delivered to the system and determine losses in the transformers turned inductors. The SHARK 200 power meter is connected to a computer and data is recorded using the COMMUNICATOR EXT. software. One can record L-L, L-N currents and voltages. It also records phase angles and power. It is expected that around 80-85% of the power is lost in the inductor as losses. Additionally, there should be a large amount of reactive power as the power factor should be near 0 as no capacitor is used.

Figure 50: Shark 200 meter [61]

Along with the power meter a voltmeter and clamp current meter was also used to determine the current and voltage at the plasma torch. This reading is a true measure of electrical energy being fed into the plasma; the difference between this and the power measured at the wall is the amount of power lost to in the power supply. These losses can

be minimized by improving the power factor and using actual inductors in opposed to using one side of a transformer as an inductor.

7.4.3 Evaluation and discussion

Mark IV exceeded expectations and provided consistent yields between 6-9% at atmospheric conditions. This is well above the objective that was expected from sub-atmospheric runs. The system works perfectly with the main limitation on run time being the overheating power supply which is extremely inefficient. Mark IV is the final revision of the reactor that will be made for this study. The final detailed reactor description along with the data for MARK IV will be presented in the results section of the thesis.

8 UNB Reactor experimental procedure

8.1 Plasma torch assembly and ignition

The plasma assembly and ignition procedure for Mark IV are as follows:

1. The three vertical brass electrodes with built-in shell and tube water cooling are inserted into the G-10 flange.
2. The heat shields to protect the G-10 are inserted following which the three coplanar graphite electrodes (adapter + holder + nub) are assembled by screwing them on to the brass electrode such that a gap of a ¼ inch is maintained between the nubs at the center.
3. The torch is then inserted and secured in place into the bottom graphite chamber of the reactor with top of the G-10 surface sealing onto the water-cooled stainless-steel flange of the reactor body.
4. The next step is to attach the water-cooling lines, air inlet from the powder feeder and the electrical wires from the power supply. Make sure none of the brass electrodes are touching the other as this can lead to arcing outside the reactor. The leads from the oscilloscopes are also attached to a pair of electrodes.
5. Flow on the water-cooling lines is tested and adjusted using a manual flow controller to allow sufficiently and even flow (~ 0.2 GPM) to each of the electrodes.
6. Ensure that the outlet air valve is open

7. Plasma gas (Ar / He) through the Tekna Nanopowder feeder is fed to the reactor at the desired flowrate using the MKS flow-controller controlled via the computer.
8. Gas flow to the viewing windows is started.
9. Turn on the cooling fans for the power supply.
10. Breaker switch is turned on to supply the required power to the electrodes.
11. The three electrodes are shorted via a controlled physical contact for ignition through the top of the reactor.
12. Upon ignition, the top port is closed.

8.2 General experimental procedure for runs

The following is the overall experimental procedure for fullerene production in this study:

1. Nanopowder feeder is tested to ensure its feed rates are in accordance with the calibrations, after which the plasma gas/carbon feed tube is attached on to the torch.
2. Following the procedure above (Plasma Torch assembly and ignition), the fullerene reactor is pre-heated with argon plasma at 18 slpm until the entire inner graphite chamber wall surface temperature reached the minimum temperature of 550^{o}C as measured using a K-type thermocouple. It typically required around 20 min to achieve the desired temperature. This is done to limit the loss of product to the wall by condensation which would then lead to the destruction of the product because of exposure to UV light.
3. After extinguishing the plasma, the power supplies are allowed to cool, and the reactor was re-ignited for the feed-run under helium at a controlled flowrate following the procedure outlined under plasma torch ignition.
4. After 30 s of sustaining stable plasma—noted by stable input current reading of 150 ± 20 A at 40 ± 10 V (line to line) reading immediately before the torch—Nanopowder feeder is turned on with sonication.
5. Feeding is stopped after run time, and plasma remains lit for an additional 30 s with feeder under sonication to make sure all the carbon remaining in the feed line is fed into the plasma.

6. Plasma is extinguished by switching the main breaker off.
7. After purging the reactor at 25 slpm for 5 min to allow all aerosolized carbon particles to filter out, the collection chamber is taken off the reactor for product soot extraction.
8. Soot was collected simply by brushing the filter and the collection chamber.

9 Soot purification testing and proof of concept design

9.1 Preliminary test

Fullerenes undergo continuous sublimation starting at 350°C however the vapor pressure only reaches substantial values above 500°C. There is no data available stating the optimum temperature for sublimation to achieve maximum transfer from solid to vapor over a period of 1 hour. Subliming the materials at a higher temperature than necessary would lead to higher energy consumption and more losses. High temperatures also increase reactivity and may lead to loss of material. To determine the optimum temperature and rate of sublimation fullerene mixture is tested using a TGA. In this, a small sample of the soot is subjected to a given temperature, and the weight loss is recorded as a function of time.

9.2 Sublimation setup

Once the optimum temperature is determined using the TGA, it was necessary to determine whether fullerenes could be extracted from the soot using sublimation, to do so an experimental set up using a 1-inch Lindberg tube furnace was set up as shown.

Figure 51: 1-inch tube furnace setup [46]

Soot from the reactor was analyzed using an HPLC and around 200 mg of the fullerenic soot was put into a ceramic crucible, which was then loaded into a 1” diameter quartz tube. The furnace was pre-heated to the optimum temperature under inert helium atmosphere flowing at 5 SCCM. A K-type thermocouple was used to monitor and control the temperature. After an hour of heating, the tube furnace was turned off, and the sample was allowed to return to room temperature for safe collection. The remaining soot in the crucible was removed from the quartz tube and analyzed using the HPLC [62].

9.3 Hot gas filtration set up

The next step was to determine whether the sublimed fullerene was able to pass through a filter and separate itself from the solid soot. To simulate this a sublimator with a filter and collector was designed and assembled using a 6-inch tube furnace as shown below.

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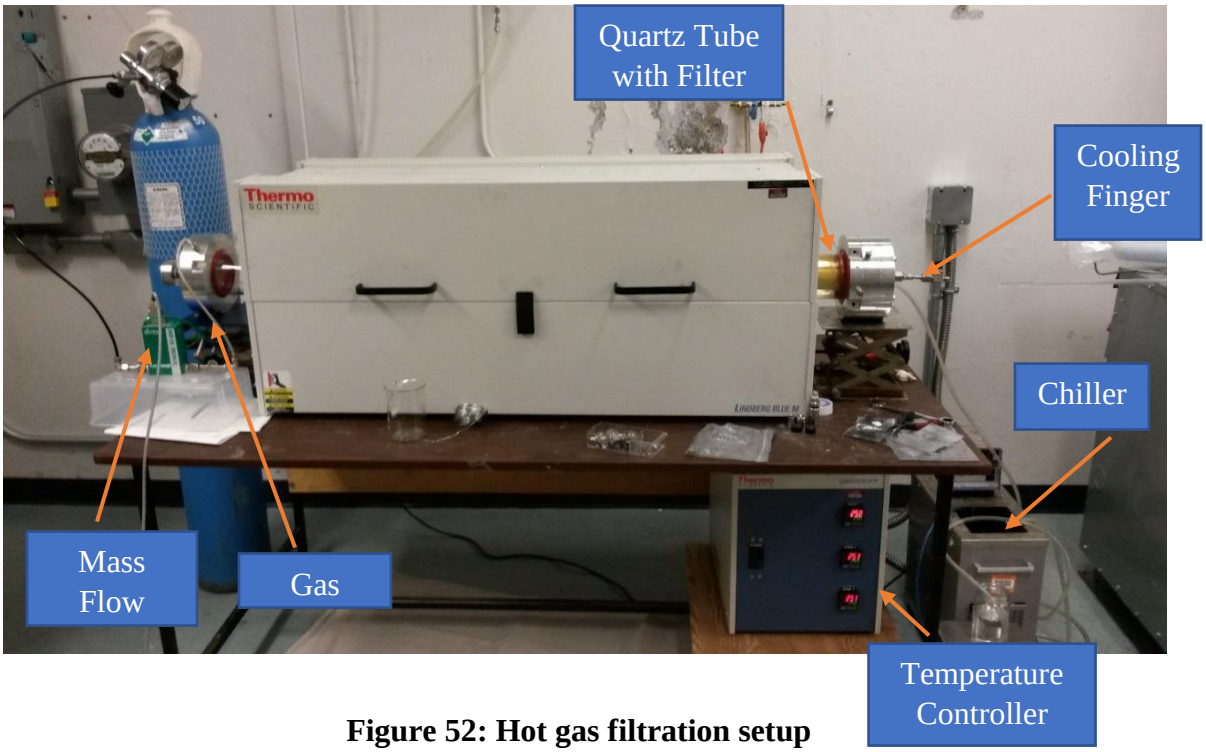


Figure 52: Hot gas filtration setup

A mixture of unreacted carbon and fullerene was placed in a ceramic crucible which was then loaded into the 6inch furnace at the optimum temperature under an inert atmosphere. The fullerene was expected to sublime and pass through the filter and deposit onto the cooling finger. This test was carried on for an hour following which if any material was collected on the cooling finger it would be analyzed.

10 Quantitative and qualitative analysis

This chapter describes the instruments used to quantitate fullerene yield, fullerene distribution and parameters for sublimation.

10.1 High-performance liquid chromatography

Figure 53: HP 1090 series II HPLC

The HPLC instrument shown above (Figure 53: HP 1090 series II HPLC) is used for quantitative and qualitative analysis of fullerenes.

An HPLC is used to separate different species in a mixture by sending a known amount through a stationary phase where based on their affinity to the material in the column they adsorb to different extents. A mobile phase is used to desorb these species thus resulting in different elution times. After they exit the column, the separated eluate

goes through a detector which is a photodiode array detector, capable of detecting absorbed wavelength in the UV-Vis region.

The HPLC is calibrated using standards, and a calibration curve is created thus allowing us to determine not just the species but also the concentration of the species in the sample. Soot samples are prepared using the following procedure

Sample preparation:

1. Soot from the reactor is dissolved in 1,2,4-trimethylbenzene (TMB) typically 20mg of soot in 5g of TMB.
2. This solution is then sonicated at room temperature for 30mins.
3. The sonicated solution is then centrifuged at ~2400 rpm for 20 mins to separate the undissolved particles to settle down.
4. The supernatant is then put into amber colored glass vials for the HPLC.

Once the sample is prepared, it is then sent through the HPLC operating at the following parameters

HPLC Operating Parameters

Mobile Phase: 1,2,4 trimethylbenzene; flow rate: 1.000 mL/min

Column: COSMOSIL 5PBB packed column

Pressure: 130 bar

Temperature: 24^0C

Sample Injection Volume: 25.0 µL

Detector: Photodiode array detector

Run time: 10 minutes

A typical chromatogram is shown below. By determining the area under each peak and using the calibration curve, the exact concentration of each species is calculated which is then used to determine yield in the initial soot sample.

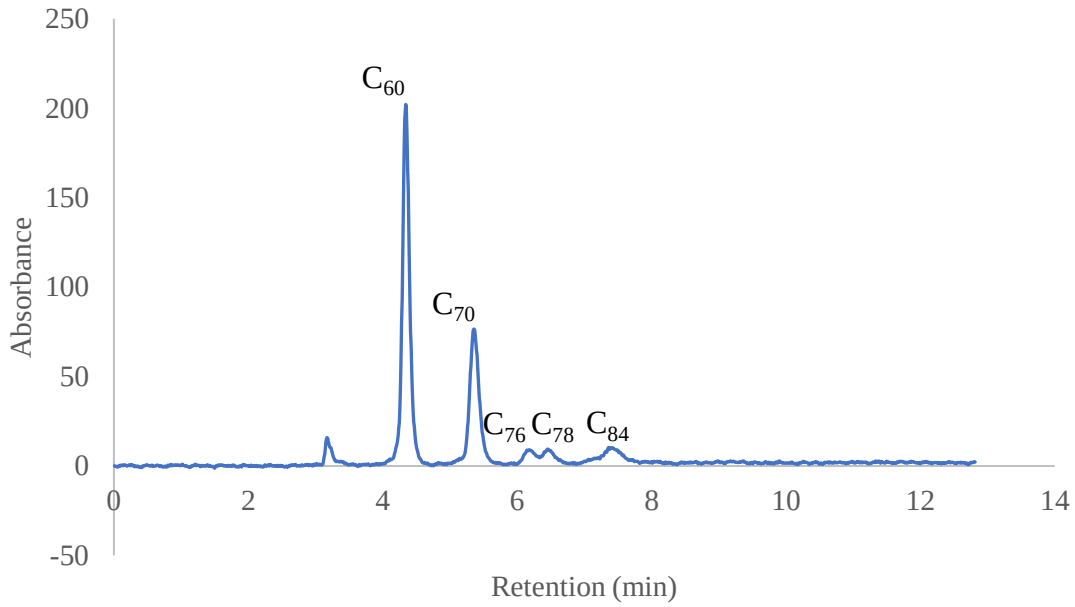


Figure 54. A high-pressure liquid chromatogram of an experimental soot sample

10.2 Thermo-gravimetric analyzer

Figure 55: Thermo-gravimetric analyzer Q50 [63]

A Thermo-gravimetric Analyzer manufactured by TA Instruments is used to determine the best sublimation temperature for fullerenes over a period of 1 hour. TGA is a device used to do thermal analysis in which the mass of a sample is measured over time as the temperature change/remains constant. It is a precision instrument and can be used to detect phase changes, thermal decompositions and gas-solid reactions. We use the TGA for solid-gas transitions to do so a known sample is put into the pan, and the furnace is heated to the required temperature at 50^0C/min and is held there for a given time, the mass loss is recorded over time elapsed. A typical TGA is shown in Figure 56: Sample TGA.

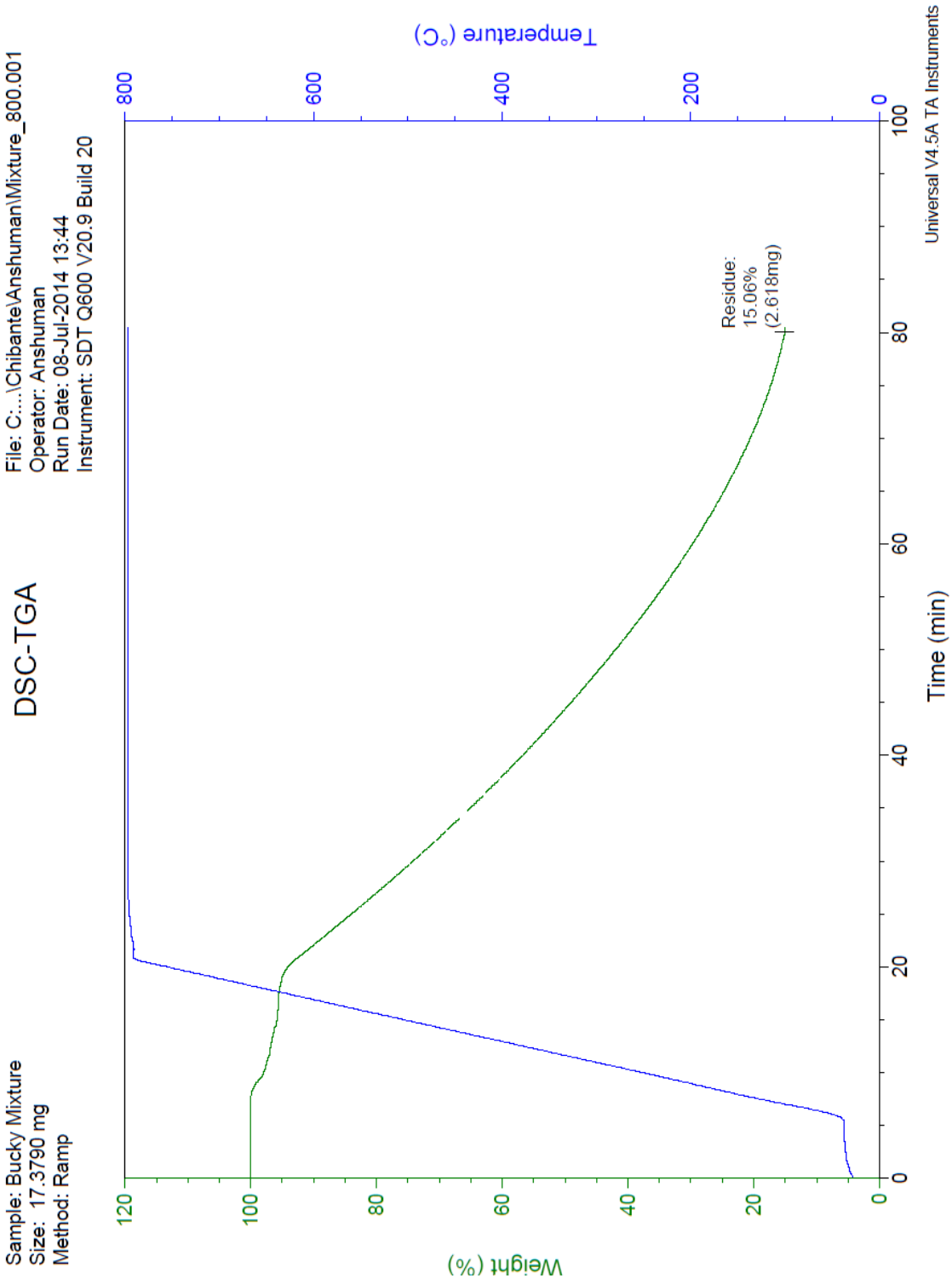


Figure 56: Sample TGA

11 Assumptions

The following assumptions are made:

1. All the carbon fed goes through the plasma
2. The plasma is in a steady state, and the power remains constant over the duration of the experiment
3. The power measured at the torch is the plasma power, and any losses in the transformers and inductors would not be considered as a part of the economic analysis as we know this power supply is not complete.
4. Reactants and products do not react with any material of construction in the process
5. The electrode erosion is negligible, and the carbon eroded is insignificant in comparison to the carbon fed in
6. The soot collection efficiency is relatively low in the short runs due to a design limitation; however, when a vacuum is used at the end, a collection efficiency of >95% is achieved. If longer runs are done, collection efficiency will improve even without a vacuum. It is assumed that the yield of fullerenes in the soot is a representative of the yield at 100% collection
7. All fullerenes in the soot samples dissolve completely in the solvent while testing for yield
8. The HPLC Calibration curve for C_{76}, $C_{78,}$ and C_{84} are the same as the calibration curve for C_{70}

12 Scope and limitations

The research will be focused on the synthesis of fullerenes using a thermal plasma. The main objective of this research is to design a pilot-scale plasma reactor which can be scaled up to produce fullerenes commercially.

G10 used to hold the plasma torch together has a low operating temperature ~130^0C thereby requiring additional heat shields and a minimum gas flow rate of 10 SLPM of the carrier/plasma gas to ensure torch stability.

The inductors used are the secondary side of three off the shelf transformers which account for major losses. Since no capacitor bank is used in parallel the reactive power is extremely high which results in overheating of the transformer. This overheating is counteracted by using external fans to keep them cool and monitored using a thermal camera; however, the run time is limited to a maximum of 20minutes depending on the plasma gas. Between each run, a 15-20-minute cooldown is required. The power will not be changed (i.e. inductance will be kept the same) through all the experiments.

The electrode nubs need replacement after each run thus the plasma torch needs to be removed, this allows for air to diffuse in and contaminate the inner surfaces this is limited by always having inert gas flowing through the system thereby limiting such diffusion but not eliminating it.

The carbon used as feedstock needs to be dried in an oven prior to filling up the feeder. During the process, the carbon does get in contact with atmospheric air which adsorbs on to the carbon this is limited by heating the carbon in the feeder by flowing inert

gas thereby driving the impurities out of the system. Other carbon feedstocks will not be considered for this study.

The total amount of carbon feedstock fed in was limited by the diameter of the feed tube connecting the feeder to the torch. At higher rpm, this tube would clog thus limiting our trials to just two different feed rates. This can be modified but requires resizing of the torch and the reactor which was not feasible based on financial and time constraints.

Sublimation trials are for proof of concept only. Further design and trials would need to be conducted to determine optimal conditions.

Furthermore, the reactor would be a platform technology to produce various nanomaterials like onion like carbons, Nano titanium, Nano copper, etc. It can also be modified to produce syngas from CO_2.

This study focuses on demonstrating a novel solvent-free plasma reactor which is an efficient, economical and environmentally friendly medium to produce fullerene. The study will not focus on the optimization of the variables. A simple proof of concept for sublimation shall be provided without any detailed design or experimentation for pilot scale use.

13 Results and discussion

13.1 MARK IV final design and results

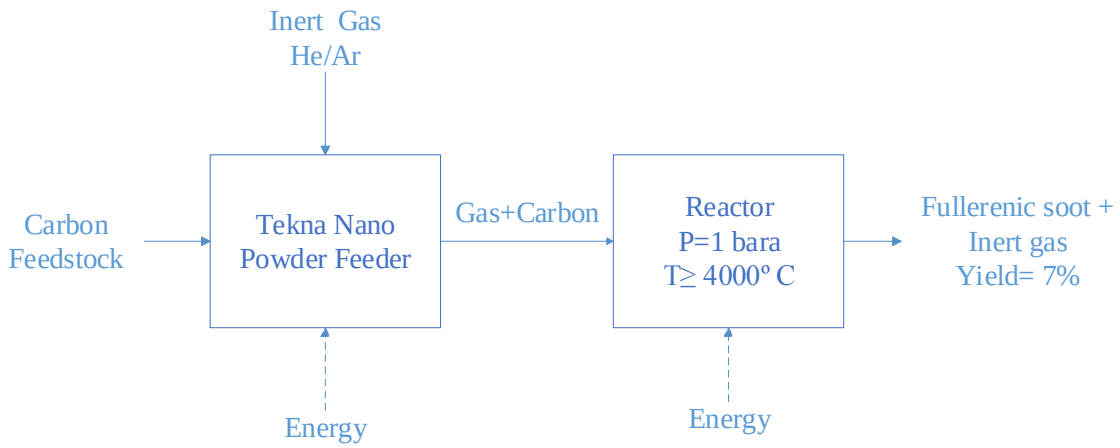


Figure 57: Flow diagram for Mark IV

Mark IV was the final iteration for reactor developed in this study. Multiple tests were carried out and the results obtained were beyond any expectation. The tests also revealed various constraints which need to be addressed if a scale-up were to take place. The final reactor design along with constraints on each part are discussed by section following which the results for yield vs carbon and gas flow rate is presented.

13.1.1 System description

13.1.1.1 Power supply

The supplied wall power (3 phase, 600 $V_{line\text{-}line}$-100 A), is dropped down to to 208 V (Line-line) with a delta 3-phase transformer and is limited to 180 A using a 4.2 mH inductor in series. Since no capacitors are used, it is a purely inductive circuit with an extremely low power factor and high reactive power. This would need fixing for a scale-up; capacitor banks would be connected in parallel to increase the power factor thereby decreasing reactive power and keeping the system small and efficient. The power meter at the wall monitors the current and voltages going into the transformer. The flow of power from each of the phases is monitored, and typically one of the phases has the opposite direction of current flow as expected. This backflow of current from the torch makes it difficult to account for power going into to the power supply however if we assume the torch to be a resistive load only 6-7 kW is being consumed by the torch. In, F1 represents a 100 A fuse, M1 is the power meter, T1 is the step-down transformer, L is 4.2 mH (secondary windings of transformer T2), and Δ represents floating ground where all three phases are connected together to cancel each other out.

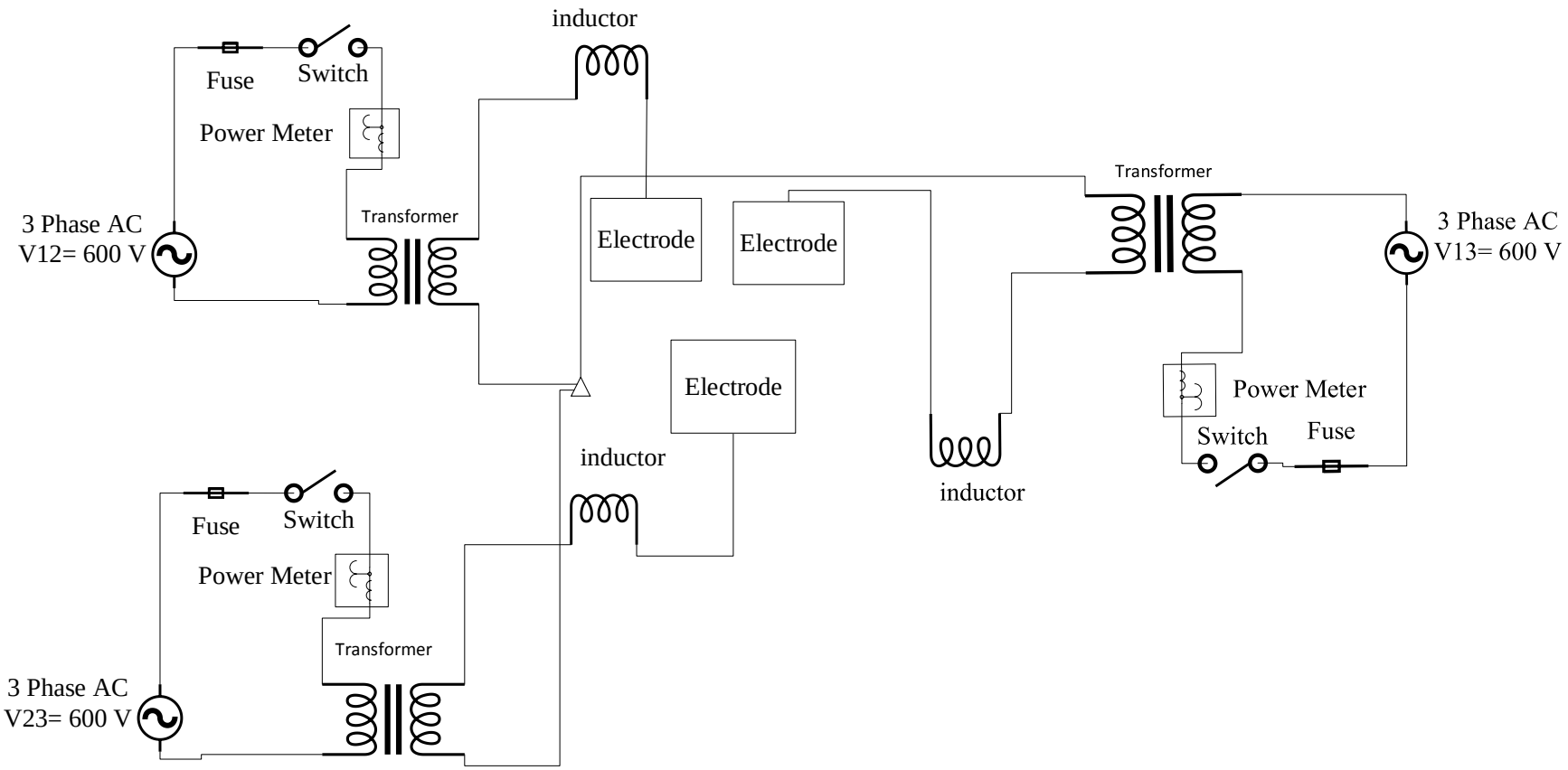


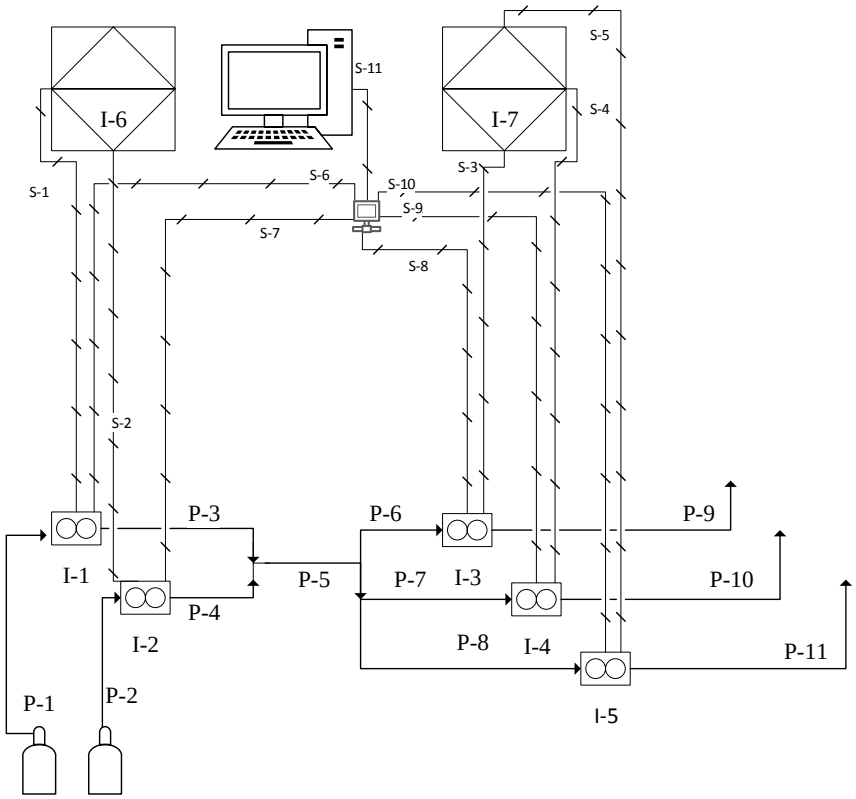
Figure 58: Mark IV power supply circuit diagram

13.1.1.2 Carbon Injection

A Tekna Nano-powder feeder is calibrated for Litx50™ (carbon black feedstock used for the study) and is used to vary the amount of carbon fed into the reactor. The feed rate was varied between 300+/-18 mg/min to 621+/-36 mg/min (5 and 10 rpm). Anything above 10 rpm led to clogging at the exit of the feeder. This could not be rectified because any increase in the outlet would mean a change to the feed tube to the plasma torch which is not possible because of the physical constraints on the torch. To scale up the torch would need redesign such that the feed tube diameter can be increased which should eliminate clogging.

13.1.1.3 Gas Handling

He/Ar is used as plasma and purge gas throughout the system. There are three places for gas to enter the system. 1) the plasma gas through the powder feeder, 2) the purge gas at the windows to keep them clean, and 3) gas from the top of the reactor to direct gas flow and to help quench the reaction. Each of these is independently controlled via MKS mass flow controllers calibrated at 25^0C and controlled via the computer. Figure 59: Gas flow P & ID depicts the electrical data connections (hatched line) and the piping (solid line) made to control gas flow to the reactor.



Pipeline List				
Identifier	***Description***	***Line Size***	***Design Pressure***	***Design Temperature***
P-1	Inert gas line	1/2"	2300psi	RT
P-2	Inert gas line	1/2"	2300psi	RT
P-3	Inert gas line	1/4"	2300psi	RT
P-4	Inert gas line	1/4"	2300psi	RT
P-5	Inert gas line	1/4"	2300psi	RT
P-6	Inert gas line	1/4"	2300psi	RT
P-7	Inert gas line	1/4"	2300psi	RT
P-8	Inert gas line	1/4"	2300psi	RT
P-9	inert gas line to quench	1/4"	2300psi	RT
P-10	inert gas line to windows	1/4"	2300psi	RT
P-11	inert gas line to powder feeder	1/2"	2300psi	RT

Instrument List			
Identifier	***Description***	***Connection Size***	***Manufacturer***
I-1	MKS Flowmeter	1/4"	MKS
I-2	MKS Flowmeter	1/4"	MKS
I-3	MKS Flowmeter to quench gas	1/4"	MKS
I-4	MKS Flowmeter to windows	1/4"	MKS
I-5	MKS Flowmeter to powder feeder	1/4"	MKS
I-6	Flow controller	NA	CCR
I-7	Flow controller	NA	CCR

Figure 59: Gas flow P & ID

13.1.1.4 Plasma Torch

The plasma torch consists of the G-10 flange, water-cooled brass electrodes, graphite adapters, graphite holders, graphite nubs and the heat shield. It is a compact design and works well for the current scale of the reactor. It is modular and easy to assemble. The nubs are consumable, but once the plasma is lit, they do not limit the run time. In order to increase the carbon feed rate to the plasma a redesign would be necessary, and it would require bigger electrodes with better cooling in a larger chamber with a better power supply for higher currents.

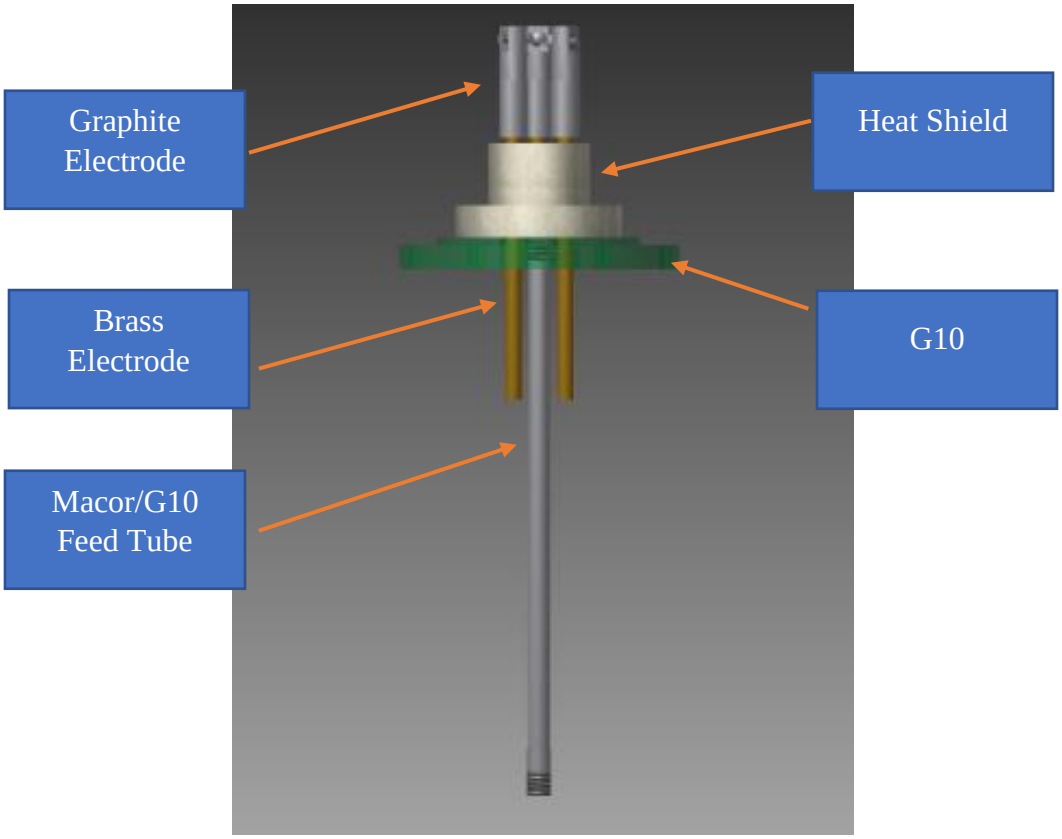


Figure 60: Mark IV plasma torch side view

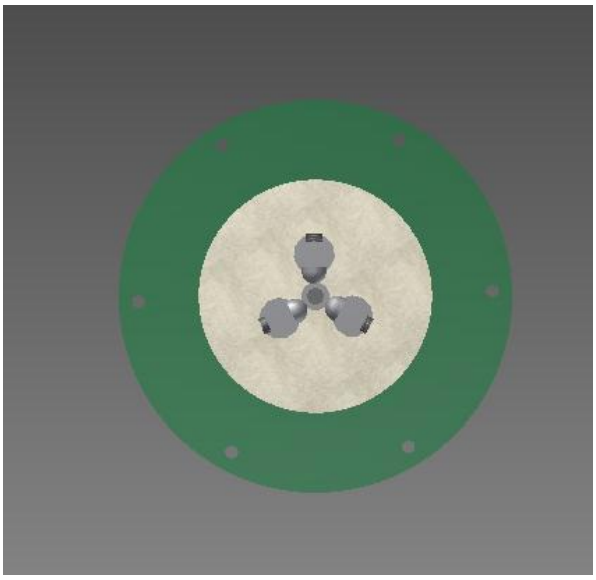


Figure 61: Mark IV plasma torch top view

Figure 62: Plasma torch after electrode failure

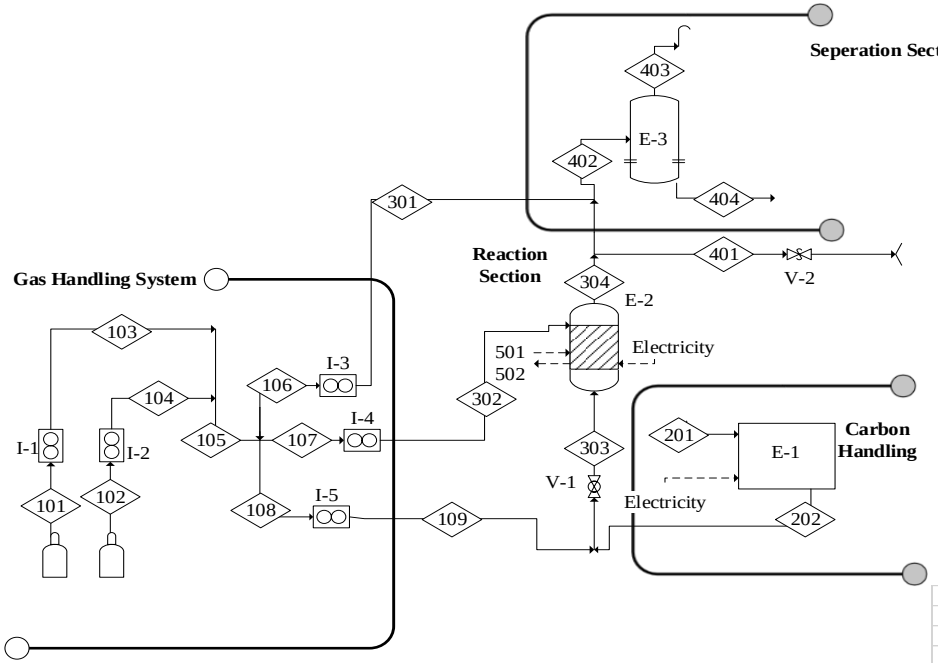
Figure 61: Mark IV plasma torch top view shows the limited space for increasing the diameter of the feed tube while Figure 62: Plasma torch after electrode failure shows the plasma torch after electrode failure in the reactor when helium gas flow below 10 slpm was tested.

13.1.1.5 Reactor Design

The new design seems to work well; however, if a new reactor were to be designed an additional gas flow should be introduced tangentially to aid the soot to stay as an aerosol until it reaches the baghouse.

13.1.1.6 Controls and Data Acquisition

LabVIEW is currently used for data acquisition. A basic set up for thermocouple data acquisition and calibrated. Along with this power was monitored using Communicator Ext software by Shark and gas flow was controlled using an intranet set up to use MKS control page. The power supply temperature was monitored manually using a thermal camera. Ideally, all these can be automated into LabVIEW and would eliminate the need for different control software making it more user-friendly.



MARK IV Process Flow Diagram

Legend	
1XX	Gas Handling
2XX	Carbon Handling
3XX	Reactor Section
4XX	Separation Section
5XX	Cooling Utilities

Instrument List			
Displayed Text	**Description**	**Connection Size**	**Manufacturer**
I-1	MKS Flowmeter	1/4"	MKS
I-2	MKS Flowmeter	1/4"	MKS
I-3	MKS Flowmeter for Quench gas	1/4"	MKS
I-4	MKS Flowmeter to Windows	1/4"	MKS
I-5	MKS Flowmeter to Powder feeder	1/4"	MKS

Equipment List				
Displayed Text	**Description**	**Manufacturer**	**Material**	**Model**
E-1	Tekna Nanopowder Feeder	Tekna	S.S	
E-2	MARK IV Plasma Reactor	Applied Nanotechnology Lab	Steel	Mark IV
E-3	Gas Filter	Applied Nanotechnology Lab	Steel	Mark IV

	Gas Handling System									Carbon Handling		Reaction Section				Separation Section				Cooling Utilities	
	101	**102**	**103**	**104**	**105**	**106**	**107**	**108**	**109**	**201**	**202**	**301**	**302**	**303**	**304**	**401**	**402**	**403**	**404**	**501**	**502**
Size	1/2"	1/2"	1/2"	1/2"	1/2"	1/4"	1/4"	1/2"	3/8"	1/2"	3/8"	1?4	1/4"	1/4"	2"	1/2"	2"	1/2"	-	3/8"	3/8"
Schedule	40	40	40	40	40	40	40	40	40	40	40		40	40	5	40	5	40	-	-	-
Phase (gas,liquid,solid)	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Solid	Solid	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Solid	Liquid	Liquid
Temperature (K)	300	300	300	300	300	300	300	300	300	300	300	300	300	320	373	373	300	300	300	288	298
Pressure (Psig abs.)	580	580	580	580	580	580	580	580	580	14	580	580	580	580	14	14	14	14	14	-	-
Gas Volumetric Flow (L/min)	17	-	17	-	17	4	1	12	12	-	-	4	1	12	13	-	17	17	-	-	-
Total Mass Flow rate (g/min)	2.8	2.8	2.8	-	2.8	0.7	0.1	2	2	-	0.48	0.7	0.1	2.28	2.38	-	3.08	2.8	0.28	3.8	3.8
Carbon Black (g/min)	-	-	-	-	-	-	-	-	-	-	0.28	-	-	0.28	0.26	-	0.26	-	0.26	-	-
Fullerite (g/min)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.02	-	0.02	-	0.02	-	-
Helium (g/min)	2.8	2.8	2.8	-	2.8	0.7	0.1	2	2	-	2	0.7	0.1	2	2.1	-	2.8	2.8	-	-	-
Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.8	3.8
			580																		

Figure 63: Mark IV process flow diagram

14 Yield vs Concentration

The concentration of the carbon in the plasma gas going in was varied between 15.78 mg/l to 62.2 mg/l of litx50 per L of helium, to achieve this gas flow rates were set to be either 10, 14 or 18 slpm while the powder feeder was set at 5 or 10 rpm.

Table 7: Reactor variable parameters

Helium Flow Rate	**Carbon Feed Rate**		**Concentration**
(slpm)	**rpm**	**g/min ±0.02**	**(g/L)**
10.0	5.0	.28	0.028
14.0	5.0	.28	0.020
18.0	5.0	.28	0.016
10.0	10.0	.62	0.062
14.0	10.0	.62	0.044
18.0	10.0	.62	0.035

The yield data obtained seemed to be constant at about 7% with the highest being 8.9% as shown in Figure 64: Yield vs Carbon concentration. Each test was repeated at least three times, and the results seem to be consistent. The constraints on the carbon injection and gas flowrate is the main reason why higher concentrations could not be tested however from literature we can expect the yield to increase until a maximum after which it is

expected to decrease as vaporization is dependent on the energy per gram of carbon feedstock [64].

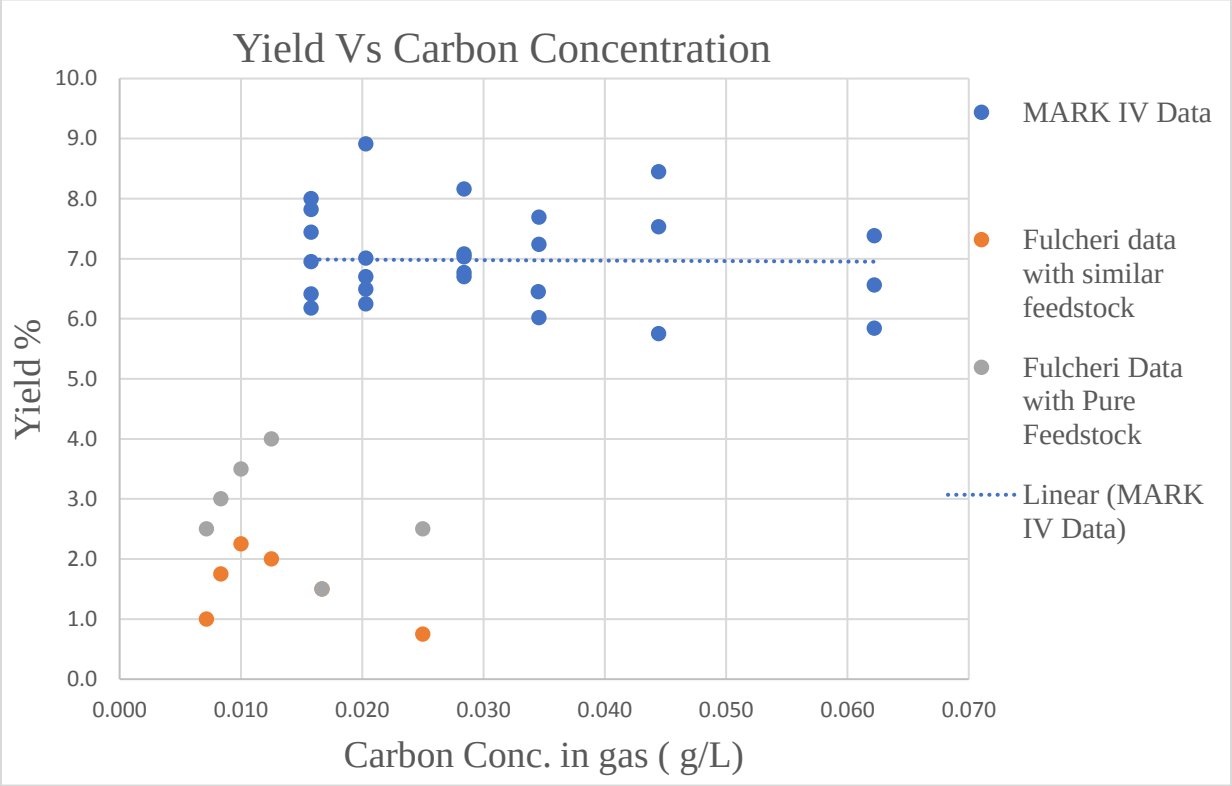


Figure 64: Yield vs Carbon concentration

Fulcheri, et al. tested for three different carbons and multiple different concentrations on their 250kVA reactor. It was determined that acetylene black was the best carbon to for fullerene production with a rate of 17 g/hr of fullerene at a yield of 4.5% represented by literature and 480 g/hr of feedstock was possible. However, the carbon feedstock used by ANL@UNB laboratory is similar to E250 grade carbon from TIMCAL which only provided a maximum yield of 2.25% (data represented in figure 64 as literature with similar feedstock) with a production rate of 5.5 g/hr at a federate of 250 g/hr. This

amounts to a specific energy input of 3.44 kW-h/gram of fullerene and 0.0756 kW-h/g of carbon feed [64]. In comparison, Mark IV as it stands (still needs optimization) has an average yield of 7% with 2.69 kW-h/g of fullerene and 0.188 kWh/g of feedstock.

The energy savings are not only limited to the plasma energy required per gram of product, but Mark IV also utilizes only 22 slpm (18 plasma+3 window+1 top quench) or 1.32 m^3/hr of total gas at its maximum while the previous technology by Fulcheri utilizes 250 m^3/hr [64]. This ~190-fold decrease decreases the operating costs of the reactor while decreasing the capital costs of the recirculation systems that would be necessary for recycling helium.

Mark IV is a smaller reactor and requires only 30 minutes of preheating at 18 SLPM of argon gas flow in comparison to the 1 hour required by Fulcheri's reactor for the walls to reach a quasi-thermal equilibrium at 20 m^3/hr. Fulcheri's reactor is water cooled thereby serving as heat sinks which would increase overall power consumption as the chillers would be needed while the only cooling on Mark IV is at the electrodes. In case of a longer run should the need for cooling arise the insulation thickness can be increased along with using the heat to preheat the gas which would improve the efficiency of the reactor.

It should also be noted that Mark IV is easy to assemble has no moving parts and can be easily constructed to be used at sub-atmospheric conditions in opposed to the older competitive technologies.

14.1 Purification

14.1.1 Preliminary TGA testing

Fullerene mixture (75% C_{60}, 25% C_{70}) is used to determine the best sublimation temperature necessary to sublime most of the fullerene from the soot. TGA was performed at three temperatures 600, 700 and 800 ^{0}C. The extract used was obtained by solvent extraction; thus only about 70-80% should sublime.

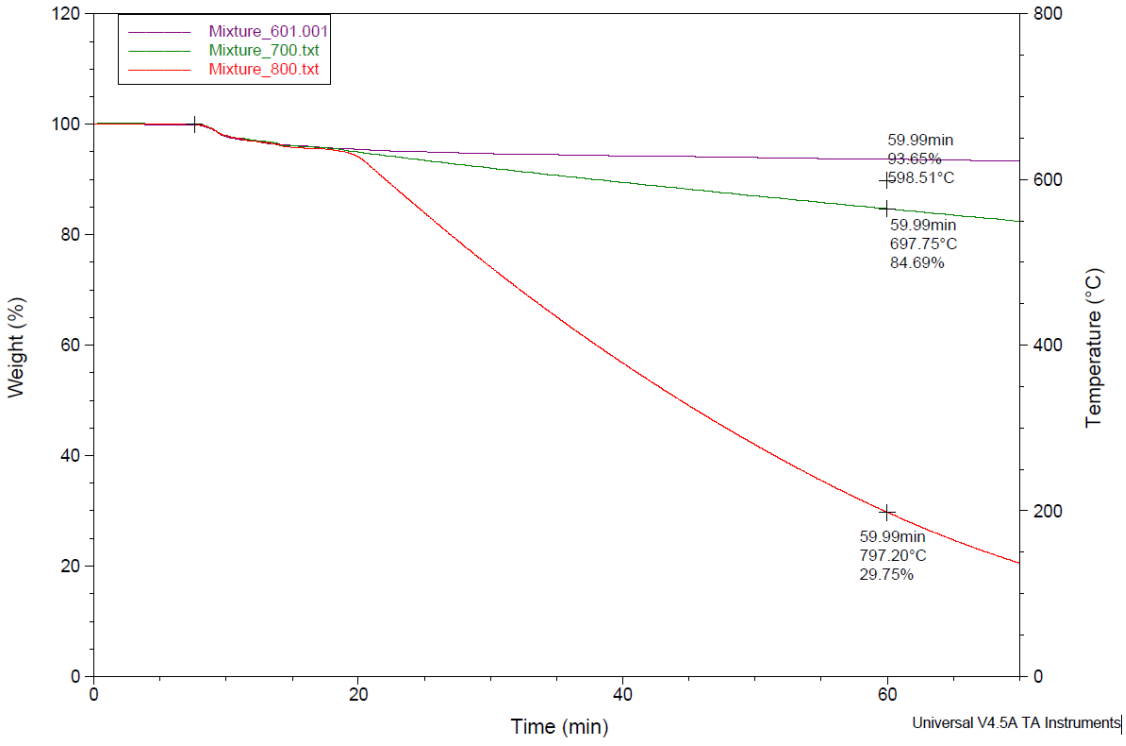


Figure 65: Preliminary TGA results

From Figure 65: Preliminary TGA results it was determined that there was a mass loss of around 4.5% in all the samples between 165 and 595^{0}C this could be the residual

solvent and PAH subliming out. This initial loss can be ignored as the soot from Mark IV would be solvent-free, analyzing the weight loss after this point would be the real determination of mass loss. At 600^0C only about 2% of the remaining 95% weight was lost over the one-hour period while at 700^0C about 10% of the extract sublimed over the same period. This was not economical as at least 70-80% of the mixture should sublime out over an hour to prove this would be a viable technique. TGA results at 800^0C depict a 65% mass loss over the hour which is acceptable and is the chosen temperature for preliminary sublimation testing in the 1" tube furnace.

14.1.2 Sublimation test

TGA testing provided a minimum temperature of 800^0C for sublimation testing; this was now further tested using actual soot from the reactor in the furnace with inert gas. Soot containing .9% of fullerenes was sublimed in the furnace with minimal argon flow, at the end of which a reddish-brown ring was noticed at the end of the reactor as shown below.

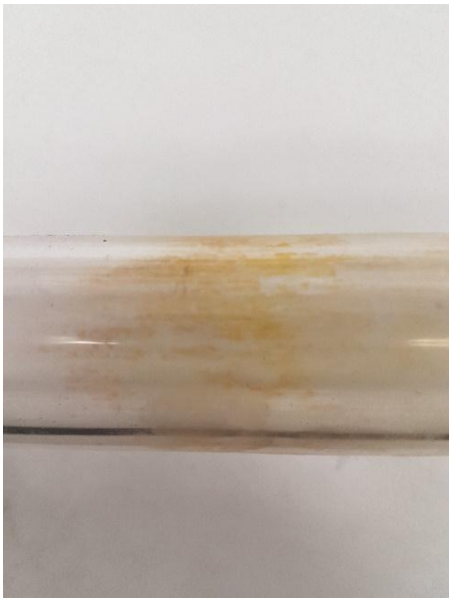


Figure 66: Brown coating on the quartz tube [62]

This ring had to be fullerenes as fullerenes do not undergo decomposition under an inert atmosphere at 800^0C. Unfortunately, there was no way to retrieve the material for further analysis as it formed an extremely thin coating, the remaining soot was tested, and it was depleted of all fullerenes as shown in Figure 67: HPLC before and after sublimation. This was a visual experiment as a proof of concept [62].

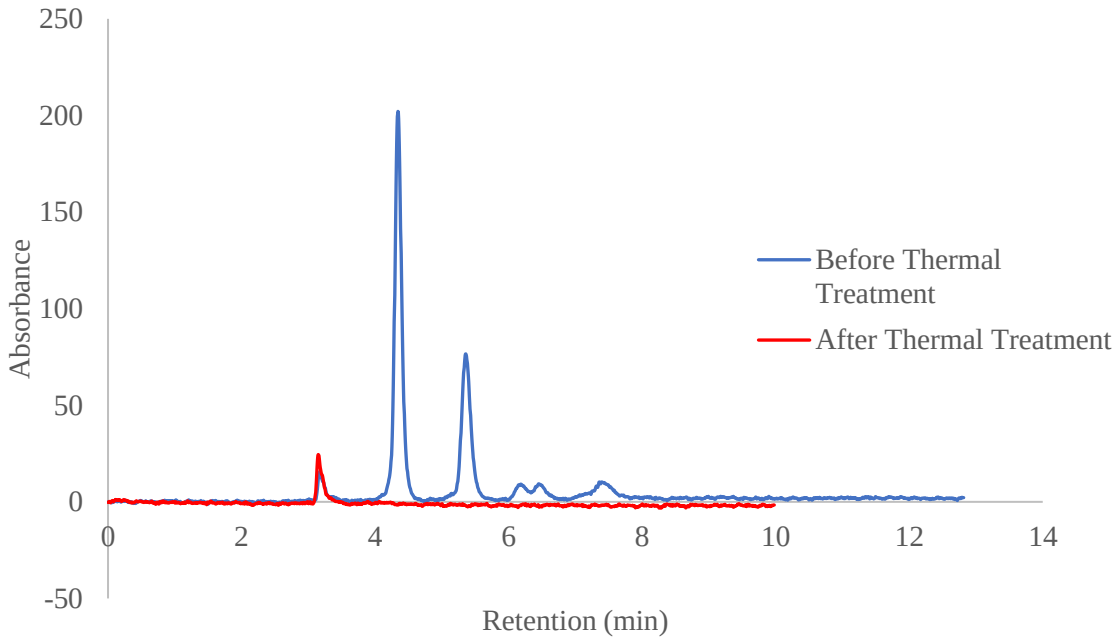


Figure 67: HPLC before and after sublimation [62]

These experimental data, along with data cited in literature, is sufficient proof of the ability to sublime fullerenes. If fullerene vapor can pass through a heated filter is not yet demonstrated. There are no studies for the same and since it plays a crucial role in the separation of fullerene vapor from the unreacted carbon another visual experiment was set up using a larger furnace and a filter.

14.1.3 Extraction testing

The separation of fullerene vapor from soot is a crucial part of the process. It needed to be tested before a full-scale sublimation system is designed. A lab-scale stationary tube furnace was modified to act as a sublimator along with a Pyrotex KE filter from BWF Envirotec. The filter has a high operating temperature of 850 ^{0}C and a high air permeability

of ~150 l/ (dm^2 min) at 200 Pa gauge. The total filter area is 0.17 m^2 which is sufficient for the proof of concept. The test for this was carried out using about 1.6 grams of fullerene mixture which was placed in ceramic crucibles inside the chamber. The furnace was heated to 700^0C and not 800^0C to limit the load on the chiller for the cooling finger.

At the end of the experiment, a reddish- brown coating was found on the cold surface just outside the furnace just like the sublimation testing.

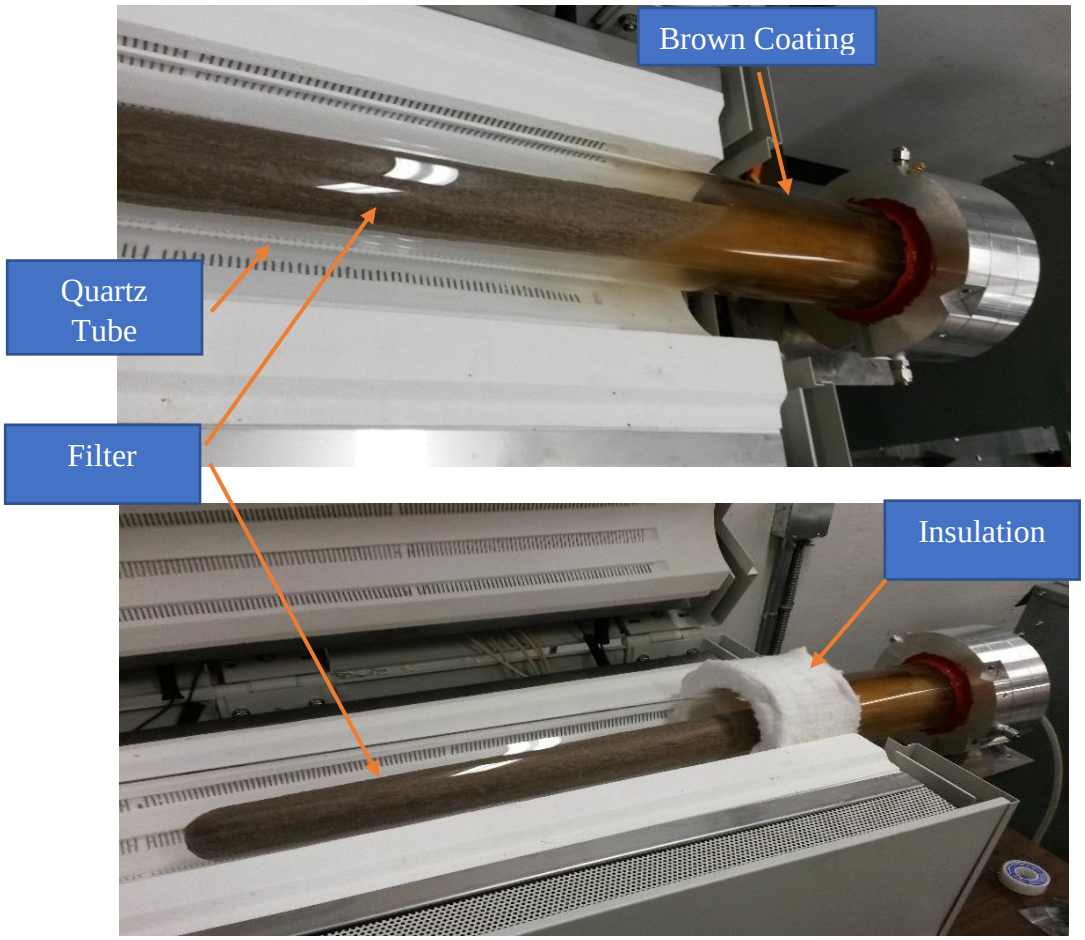


Figure 68: Fullerene separation setup

The cooling finger also had some deposit which looked like fullerene powder. This was scraped and dissolved in toluene to test for fullerenes. The remaining sample in the crucible was weighed in at 1.24 g. There was a 25% loss in weight which was in line with the TGA results obtained.

Figure 69: Cooling finger with fullerene deposit

Figure 70: Fullerene dissolved in 1,2,4-Trimethyl Benzene after sublimation

Each of the four-sample tested positive for fullerenes proving that separation through a fine air filter is a valid solvent-free method. If the technique is to be used industrially, further testing with collected soot and optimization of design, temperature, and flowrates are required.

14.2 Fullerene production process cost estimation

The primary objective of this project is to drop the cost of sublimed fullerenes to aid market growth while making sure the product is 100% solvent-free. To evaluate the scalability of the process a preliminary economic analysis is conducted for a pilot plant with a 10X multiplier of the current capacity. The analysis is for a pilot-scale facility based on our current reactor and represents the quickest way forward to pilot scale production from the current scale. At this new scale, one would be able to analyze other variables such as pressure and power input to the plasma while doing an actual assessment of the feasibility on the larger industrial scale. The sole purpose of this analysis is to determine whether we see a reduction in price at this scale because if so then it would definitely result in cost reduction on the industrial scale as labor and raw material should be the biggest costs as in any process plant, and they do not increase linearly with plant capacity thereby reducing production cost per unit as capacities increase.

The economic analysis was conducted considering two scenarios:

1) Production without raw material recycling
2) Production with raw material recycling

When considering production without raw material recycling, we assume that all the helium exiting the reactor and sublimator is vented to the atmosphere without any recovery and all unreacted carbon black is sent to the landfill or sold as thermally treated carbon to other industries (the value of this byproduct value is 0 CAD for this analysis). This process is depicted in the block flow diagram in Figure 71: Block flow diagram for fullerene production without recycling.

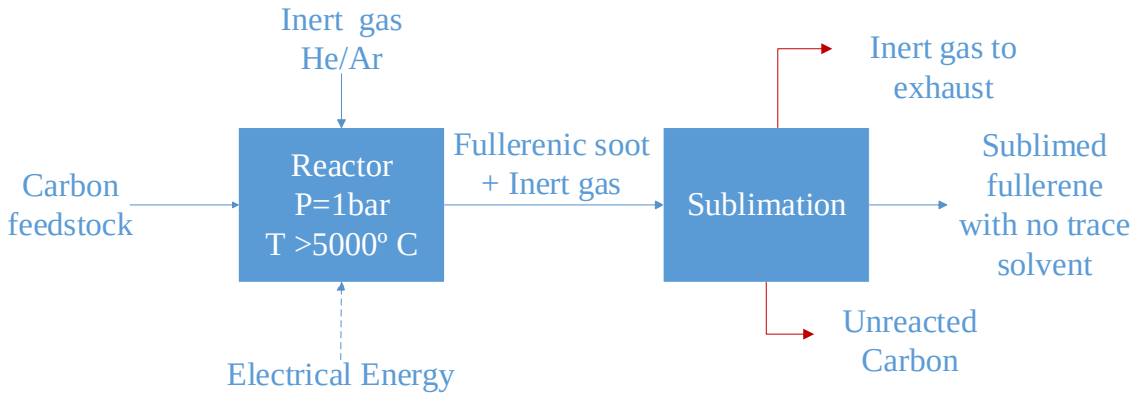


Figure 71: Block flow diagram for fullerene production without recycling

The second scenario is the actual proposed process in which the helium and unreacted carbon are recycled back into the system as shown in Figure 72: Block flow diagram for fullerene production with recycling. Helium has a 99% recycle efficiency while carbon has a 90% recycle efficiency for this analysis. This would mean additional capital costs for recycling systems however lower annual operating costs.

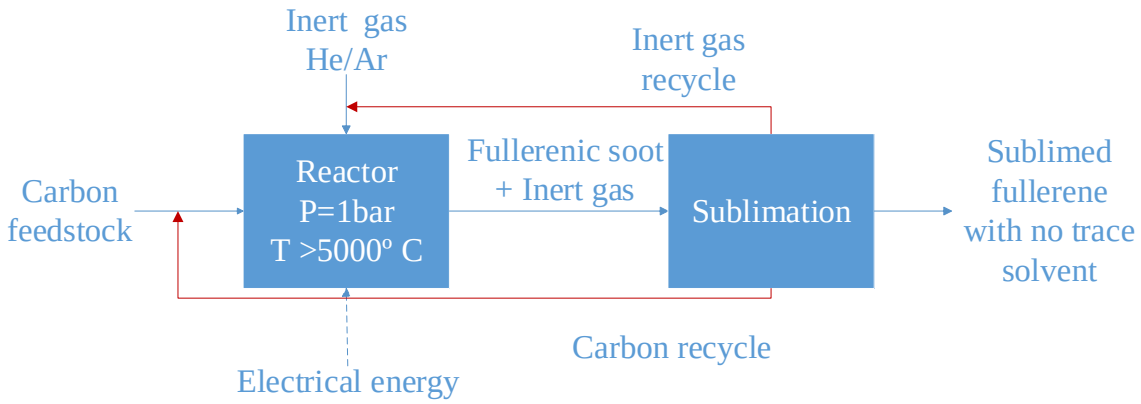
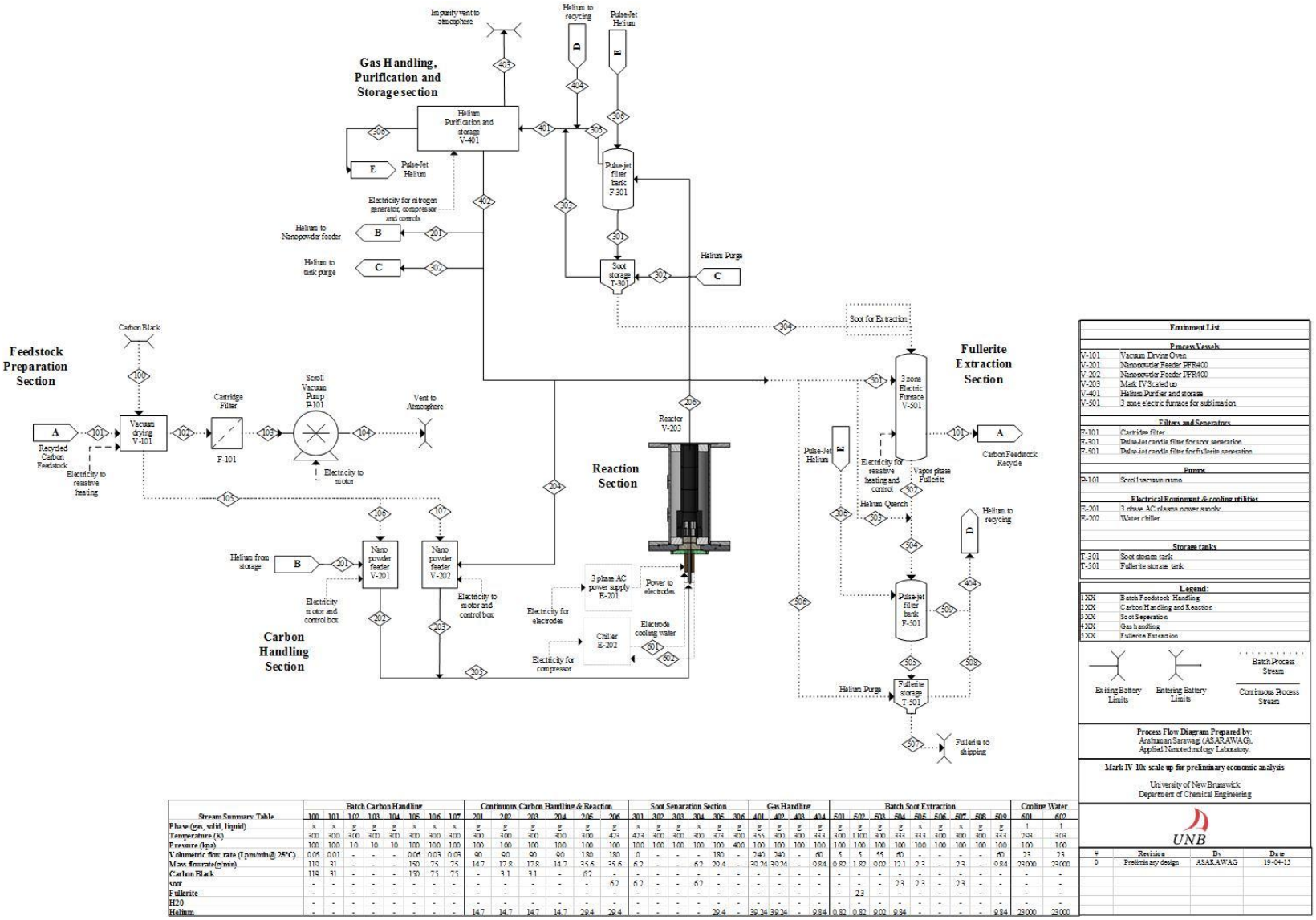


Figure 72: Block flow diagram for fullerene production with recycling



Stream Summary Table	Batch Carbon Handling								Continuous Carbon Handling & Reaction						Soot Separation Section						Gas Handling				Batch Soot Extraction								Cooling Water	
	100	101	102	103	104	105	106	107	201	202	203	204	205	206	301	302	303	304	305	306	401	402	403	404	501	502	503	504	505	506	507	508	509	601	602
Phase (gas, solid, liquid)	s	s	g	g	g	s	s	s	g	g	g	g	g	g	s	g	g	s	g	g	g	g	g	g	g	g	g	g	s	g	g	g	g	l	l
Temperature (K)	300	300	300	300	300	300	300	300	300	300	300	300	300	473	473	300	300	300	373	300	355	300	300	333	300	1100	300	333	333	300	300	300	333	293	303
Pressure (kpa)	100	100	10	10	10	100	100	100	100	100	100	100	100	100	100	100	100	100	100	400	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Volumetric flow rate (Lpm/min@ 25°C)	0.05	0.01	-	-	-	0.05	0.03	0.03	90	90	90	90	180	180	0	-	-	-	180	-	240	240	-	60	5	5	55	60	-	-	-	-	60	23	23
Mass flowrate(g/min)	110	31	-	-	-	150	75	75	14.7	17.8	17.8	14.7	35.6	35.6	6.2	-	-	6.2	29.4	-	39.24	39.24	-	9.84	0.82	1.82	9.02	12.1	2.3	-	2.3	-	9.84	23000	23000
Carbon Black	110	31	-	-	-	150	75	75	-	3.1	3.1	-	6.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
soot	-	-	-	-	-	-	-	-	-	-	-	-	-	6.2	6.2	-	-	6.2	-	-	-	-	-	-	-	-	-	2.3	2.3	-	2.3	-	-	-	-
Fullerite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.3	-	-	-	-	-	-	-	-	-
H20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Helium	-	-	-	-	-	-	-	-	14.7	14.7	14.7	14.7	29.4	29.4	-	-	-	-	29.4	-	39.24	39.24	-	9.84	0.82	0.82	9.02	9.84	-	-	-	9.84	23000	23000

Figure 73: Mark IV scale up PFD

A revised process flow diagram for the 10X scale up is shown in Figure 73: Mark IV scale up PFD. In this scale, up the feedstock preparation section and soot extraction processes would be batch processes as the scale does not warrant a continuous operation. The feedstock preparation section comprises of a vacuum drying (V-101) which is used to remove any adsorbed gases/moisture from the carbon black feedstock. This oven is pumped down using a scroll pump (P-101) through a cartridge filter (F-101) to ensure no particulates are being sucked out. Once the feedstock is cleaned, it is fed into two nanopowder feeders from TEKNA, model: PFR400 (V-201, V-202). These feeders have conical hoppers which can hold carbon in an inert environment before it is aerosolized using a carrier gas (stream 201,204).

This aerosolized carbon feedstock in an inert gas (helium) for both feeders is then combined (stream 205) and fed to the 10X reactor. The reactor has a 10 litre capacity, the electrodes in the reactor are connected to a 10.9 kW cooling capacity chiller and a 3-phase ac power supply. Stream 206 exits the reactor at 423 K containing carbon soot which has 7% fullerenes and enters a pulse jet filter bank. This filter bank has a minimum cloth area of $4m^2$ for a flow rate of 210 slpm, here the solid soot is separated from the inert gas and sent to storage tank T-301. Helium is sent to helium purification and storage. Helium purification is done using cryogenic purification to >99.8% which is then stored as liquid helium in tanks. The pilot plant will have stores for about two days supply of helium.

Once enough soot is formed it is fed to a 3-zone electric furnace for fullerite (mixture of C_{60}+C_{70}+higher fullerenes) extraction. The fullerenes evaporate, go through a filter, and the vapor is then cooled to room temperature using a quench gas (steam 503). This leads

to fullerene condensation to the solid phase as an aerosol in helium which is then fed to pulse jet filter where the fullerenes are separated from the inert helium. The sublimed solid fullerenes collected are stored in a tank (T-501) awaiting packaging and shipping while the helium is sent for recycling.

14.2.1 Capital investment

Total capital investment for a manufacturing facility consists of direct costs, indirect costs, start-up costs, and working capital. Direct costs are broken down into various categories namely:

1) Process Equipment Cost (PEC): which is the total cost of all equipment's delivered to the site, this was determined using estimate quotes from suppliers for all needed equipment with a few exceptions namely:
    a) Pulse jet candle filter costs were estimated using filter area and cost estimates from the literature. [65] [66]
    b) Reactor costs were scaled up from the actual costs incurred in making mark IV and using the .6 exponent method
    c) Soot and fullerite storage costs were determined using the internet for the required size.
    d) Helium purification and storage costs were obtained via a quotation and included delivery, installation, commissioning and pre-engineering costs.
2) Installation costs: This is the estimate of the total costs of assembling all the equipment's and running all safety checks prior to plant startup, it was determined using textbooks and experience from assembling Mark IV.

3) Piping cost: These include costs to install process piping, valves, fittings, supports, etc. Based on experience from Mark IV it was chosen to be only 10% of PEC
4) Instrumentation and control costs: Instrumentation is a major cost for this technology as it requires extensive controls which is why 40% of PEC was allocated for this section.
5) Electrical costs: Electrical installation includes power wiring, lighting, service and instrumentation, and control wiring. The complete installed costs of electrical are estimated to be 15% of PEC
6) Land and structure/building cost: These were not considered as I expect the pilot plant to be on a rented facility with an option to buy.
7) Service facilities: These include utilities such as water, compressed air, waste disposal, fire protection, etc. This was determined to be 20% of PEC

Indirect costs are broken into the following 4 categories

1) Engineering and supervision: These include project design and engineering, purchasing, drafting, accounting, cost engineering, communications, etc. This is usually 30% of PEC; however, since this is a nascent technology should require more work which is why 50% of PEC is chosen.
2) Construction costs: Temporary construction an operation, tools, office personnel at the construction site, travel, living, insurance, taxes, etc. This was taken as 15% of direct costs
3) Contingencies: It was estimated to be 10% of fixed capital investment

4) Legal costs: This includes lawyer fees to set up the corporation, write and execute contracts, etc. It was considered to be 2% of fixed capital investment

The addition of direct and indirect costs gives us total fixed capital investment. This is then added along with start-up costs and working capital costs to provide us with total capital investment. The startup costs include the hiring of personnel prior to plant starting, utilities, etc., it also includes 4 months security deposit for renting a 6000 sq. ft. commercial facility and setting up the office space and workshops.

Table 8: Process equipment costs shows the total equipment costs for both with and without helium/carbon recycling.

Table 8: Process equipment costs

Identifier	Equipment Name	Estimation Method	Cost	
			Without Recycling	With Recycling
V-201	Nano powder Feeder	Quote	25000	25000
V-202	Nano powder Feeder	Quote	25000	25000
V-203	Reactor	Experience + Quote	50000	50000
V-501	3-zone electric furnace	Quote	20000	20000
F-301	Pulse-jet candle filter	Textbook	44000	44000
F-501	Pulse-jet candle filter	Textbook	44000	44000
E-201	3-phase power supply	Quote	26000	26000
E-202	Water chiller	Quote	10000	10000
T-301	Soot storage tank	Internet	3000	3000
T-501	Fullerite storage tank	Internet	3000	3000
V-401	Helium purifier and storage	Quote	NA	500000
	Total equipment cost		250000	750000
	Delivery to site	10% for remote area	25000	25000
	Total Process Equipment Cost (PEC)		**275000**	**775000**

The total direct costs for both with and without recycling are shown in Table 9: Direct costs. Note that there is no increase in costs 2-5 as the only new equipment added when recycling is the helium purifier, and the cost of installation, piping, etc. is included in the quoted price.

Table 9: Direct costs

	Category	Estimation Method	Cost	
			Without Recycling	With Recycling
1	Process Equipment Cost	See Table 8	275000	775000
2	Installation Cost	Appendix D	66000	66000
3	Piping Cost	10%	27000	27000
4	Instrumentation and control	40%	110000	110000
5	Electrical	15%	41000	41000
6	Land & structure	NA	NA	NA
7	Service	20%	55000	155000
	Total Direct Costs		**574000**	**1174000**

The breakdown for indirect costs as per the procedure explained earlier is represented in Table 10: Indirect costs.

Table 10: Indirect costs

	Category	Estimation Method	Cost	
			Without Recycling	With Recycling
1	Engineering & Supervision	50%	138000	138000
2	Construction	15%	86000	176000
3	Contingencies	10%	80000	149000
4	Legal	2%	16000	30000
	Total Indirect Costs		**320000**	**493000**

Fixed capital investment is a sum of direct and indirect costs, once we add startup costs and working capital costs we obtain our final total capital investment for both scenarios of with and without recycling at 1.25 million CAD and 2.02 million CAD respectively as shown in Table 11: Total capital investment.

Table 11: Total capital investment

	Category	Estimation Method	Cost	
			Without Recycling	With Recycling
1	Direct cost		574000	1174000
2	Indirect costs		320000	493000
3	**Total fixed capital investment**	(1+2)	**894000**	**1667000**
4	Startup cost			
	Security deposit	4*15000 CAD/month	60000	60000
	Space upgrades and supplies	Appendix D	120000	120000
	Other	10%	167000	167000
	Total startup cost		**347000**	**347000**
5	**Working capital**	Appendix	**10000**	**10000**
	Total capital investment	(3+4+5)	**1251000**	**2024000**

14.2.2 Annual Operating Costs

These costs are associated with day to day operations of a plant it includes the raw material costs, utility cost, labor wages and benefits, payroll overheads, rent, maintenance cost, depreciation of assets, plant insurance and taxes. The total of this is called production cost, upon adding selling and management costs to this we obtain our annual operating costs.

The raw material and electricity utilization for both with and without recycling was determined and reported in Appendix C. The raw material costs were ~10 CAD/m^3 [67] for industrial grade helium, 15.5$/kg for carbon and 7 cents per KWH of electricity in New Brunswick [68]. These costs are translated into a table in Appendix D.

Operating labor was determined by estimating labor required to run the plant all year round; however, a 25% downtime is estimated as the technology is new and complex. It was determined that 2 operators per shift were required to run the plant at any given point, thereby requiring 10 fulltime operators at the plant to cover all shifts and accounting for vacation and sick days. It was also determined that a full-time supervisor who is cross-trained in mechanical and electrical would also be necessary for oversight and direction. The reactor has consumable parts which require machining, and it is economically beneficial to have a part-time machinist on site to streamline the process and limit costs. Operators were paid at 26 CAD/hr [69] supervisor is paid 33 CAD/hr, and the machinist is paid 35 CAD/hr respectively, their benefits were calculated as per Canadian rules [70]. Payroll overhead which includes hidden costs such as accounting, administration, etc. are estimated to be 10% of total labor costs.

Maintenance was determined as shown in appendix while the insurance and taxes for the plant were 1% and 1.08% of plant cost respectively. The addition of the above costs gives us a production cost of 2 million and 1.2 million CAD for with and without recycling. The selling and management costs were considered to be 10% of these production costs which when added to the production costs provides us our annual operating costs.

Table 12: Annual operating costs

	Category	Estimated Cost /unit	Cost	
			Without Recycling	With Recycling
1	Raw material and utility costs			
	Helium	10 CAD/Nm3	870000	9000
	Carbon black	15.5 CAD/kg	35000	**6000**
	Electricity	.07 CAD/kWh	4000	**49000**
	Total raw material and utility costs		**909000**	**64000**
2	Labor wages			
	Supervisor	33CAD/hr	70000	70000
	Operator	26CAD/hr	540000	540000
	Machinist	35 CAD/hr	36000	36000
	Total labor wages		**646000**	**646000**
3	Labor Benefits			
	Supervisor	Appendix D	11000	11000
	Operators	Appendix D	97000	97000
	Machinist	Appendix D	7000	7000
	Total labor benefits		**115000**	**115000**
4	**Total labor costs**		**761000**	**761000**
5	Payroll overhead	10% of labor	76000	76000
6	Rent (option to own)	15000 CAD/month	180000	180000
7	Maintenance	Appendix D	40000	40000
8	Depreciation	10% PEC	27000	75000
9	Insurance	1% plant cost	6000	17000
10	Taxes	1.08% plant cost	6000	18000
11	**Total production cost**	1+4+5+6+7+8+9+10	**2005000**	**1231000**
12	Selling and management cost	10% production cost	200000	116000
	Annual Operating Cost	11+12	**2205000**	**1347000**

Annual operating costs of 2.2 and 1.3 million were estimated for without and with recycling respectively, although the capital costs for the recycling option is higher the purification plant pays for itself within the first year itself.

14.2.3 Income Statement

The proposed process at the current production level can produce ~158kg of sublimed fullerene a year at 7% yield operating for 6048 hr/year (25% downtime). The retail price of a similar grade of fullerene stands between 24-102$/gram. The current cost of production is 12.7 CAD/g and 7.8 CAD/g for without and with recycling respectively, both these prices are well below our target selling price of 15 CAD/g which would undercut the market by 60% to be competitive and generate demand eventually as the market volume increases a large-scale production plant can be set up to further drop costs to 5 CAD/g as labor is a major cost of production and it does not increase linearly with scale. Provincial and federal taxes of 14% [71] and 15% [72], respectively are considered to determine a net income of .12 million and .73 million CAD annually as shown in Table 13: Income statement.

Table 13: Income statement

Category	Cost	
	Without Recycling	**With Recycling**
Hours of operation (hr/yr)	6048	6048
Reactor Yield (%)	7%	7%
Annual Production (kg)	158	**158**
Selling Price (CAD/kg)	15000	**15000**
Annual sales revenue (million CAD)	**2.37**	**2.37**
Annual operating costs (million CAD)	2.2	1.34
Net profit before taxes (million CAD)	0.17	1.03
Net Profit (million CAD)	**0.12**	**0.73**
Production Cost	2005000	1231000
(Production Cost)/g	**12.7**	**7.8**

The proposed process with recycling generates a healthy profit of .73 million annually even at a small pilot scale and is well below our target cost price of 10 CAD/g. However, the process without recycling is above our target cost price but still generates a profit of .12 million.

14.2.4 Sensitivity Analysis

Return on investment (ROI) was calculated by dividing gross annual profit by total capital investment as shown in Table 14: Return on investment.

Table 14: Return on investment

	Category	Estimate	ROI %	
			Without Recycling	With Recycling
1	Gross profit (million CAD)		0.198	1.05
2	Total capital investment (million CAD)		1.25	2.02
	Return on Investment (ROI)	**(3)/(4) %**	**16**	**52**

The proposed process in both scenarios has a good return on investment; however, when the entire process with recycling is implemented, it has a 52% ROI which is stellar. To further analyze how this ROI would change with respect to change in capital investment, raw material costs, sales price and reactor yield each of these were varied ± 15% and their effect on ROI was monitored and reported in Table 15: Sensitivity analysis without recycling and Table 16: Sensitivity analysis with recycling. As expected yield and sales price variations on ROI however when we do not use recycling we can see that a 15% drop in yield or sales price gives us a negative ROI which increases the risk of the

investment and is more visible in the tornado plot shown in Figure 74: Tornado plot without recycling.

Table 15: Sensitivity analysis without recycling

Without Recycling	ROI	
	-15%	15%
Total Capital Investment	39	11
Raw Material Cost	29	4
Sales Price	-14	49
Yield	-13	47

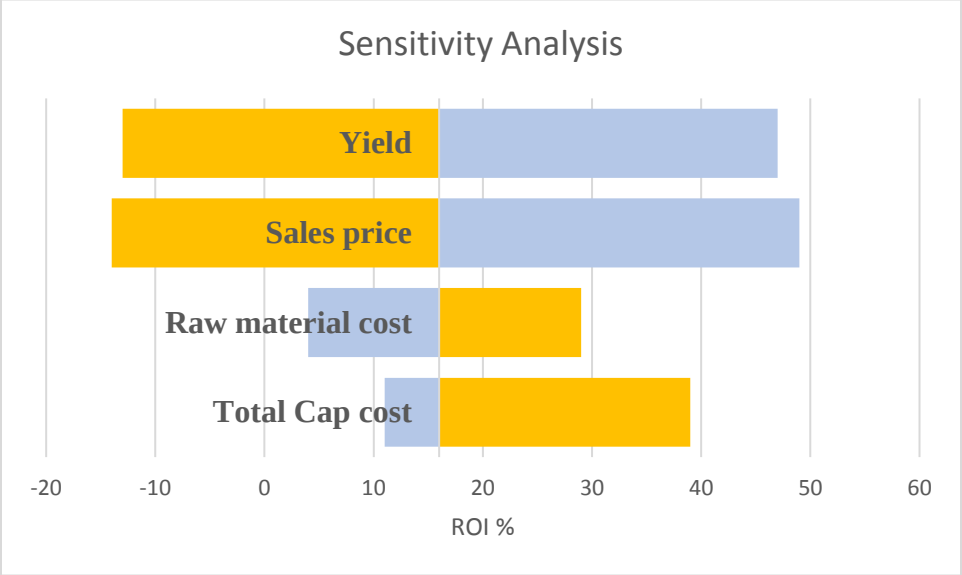


Figure 74: Tornado plot without recycling

A sensitivity analysis on the complete process with recycling shows that even though these parameters affect ROI, it still maintains a healthy ROI. Also, one can see the effect of raw material costs has been minimized with recycling which is extremely advantageous as helium is mined and the costs vary quite a bit and have only been

increasing lately. A visual representation of this can be seen in Figure 75: Tornado plot with recycling.

Table 16: Sensitivity analysis with recycling

With Recycling	ROI	
	-15%	15%
Total Capital Investment	63	43
Raw Material Cost	53	51
Sales Price	34	70
Yield	34	70

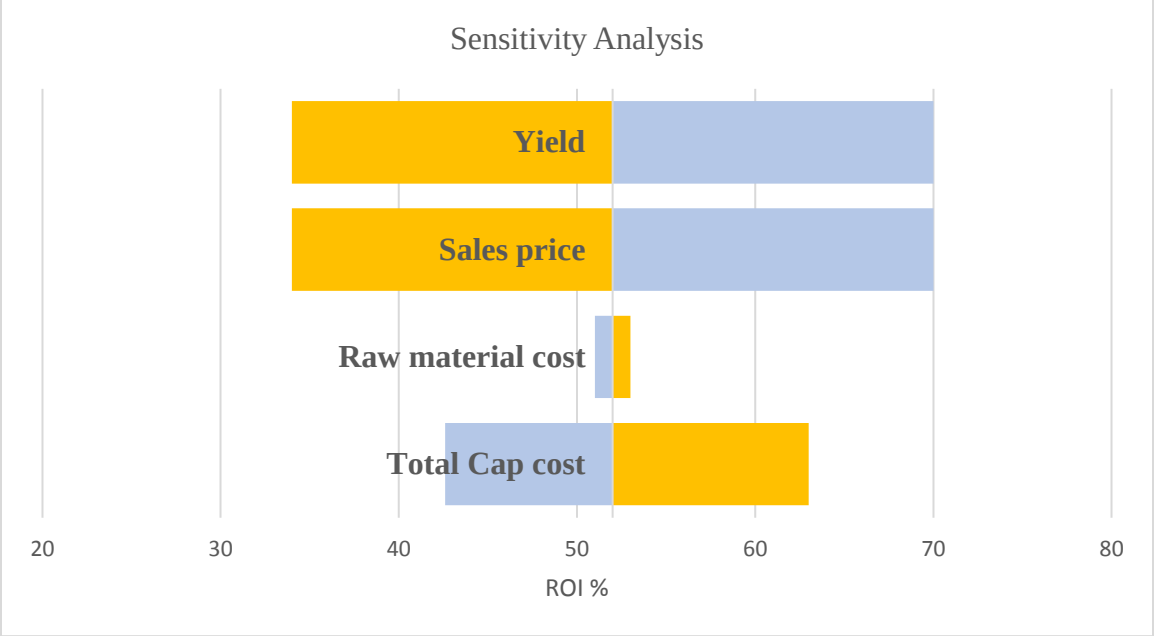


Figure 75: Tornado plot with recycling

15 Conclusion

The primary goal of this project is to produce ultra-pure fullerenes which have never been in touch with solvents in the cheapest possible manner to scale the process up for commercial production. To do so, multiple designs of the reactor have been tested from Mark I to Mark IV. The initial goal was to produce a 2% fullerene yield at atmospheric conditions and 4% at sub-atmospheric conditions. Mark III was able to achieve a 3.5% yield at atmospheric conditions which led to the development of MARK IV which provided us with an average of 7% yield consistently. This is a breakthrough as these are the highest yields reported in the literature to our understanding. The yields are comparable to the carbon arc process which is a batch process and is 7-fold better than the combustion process which is the current choice of production in the industry. Even when comparing Mark IV to similar methods in literature Mark IV outperforms them on every front such as better yields, better energy, and raw material utilization, ~200 times lower gas flow rates and operationally simple design. It would require some modifications to test the maximum capability of the reactor on the pilot scale but would then be ready for scale up to industrial scale.

The second aspect of the process after achieving the production of solvent-free fullerenes is their purification. Although most methods use solvent extraction there is little to no research in solvent-free recovery this is mainly because most of the soot produced today is from the combustion process. As a proof of concept, two different setups were tested the first one was simply to check whether it was possible to separate all the fullerene

from the soot by evaporation while the second one was to test the separation of soot from fullerene through a membrane. Both these tests were successful; however, further testing and redesigning would be necessary for testing on the pilot scale.

The Applied Nanotechnology Laboratory has proven that the solvent-free production of fullerenes is possible and a preliminary economic analysis of Mark IV and the sublimator setup would drop the cost price of fullerene to ~12.7 CAD and even further down to ~ 7.8 CAD with the implementation of carbon and gas recycling. The system would be able to produce 158 kg of sublimed fullerene mixture annually which when sold at 15 CAD/gram would generate 0.75 million CAD in net profit annually.

The fullerene reactor was also able to make onion-like carbons by changing plasma gas to argon and varying the carbon and gas flow conditions. Nano titanium and other nano-sized metals are made by vaporization and condensation of the metals. As all these metals have vaporization temperatures below that of graphite, the reactor can serve as a potential platform technology to produce various nanomaterials.

The process works, and as per our knowledge, MARK IV is the most efficient reactor for the solvent-free production of fullerenes to date. It is ready to disrupt the industry and should have a direct impact on the market growth by allowing a wider more affordable fullerene product range on the market. Hopefully, fullerenes will be the new plastic or aluminum in the life of the consumer.

16 Future Work

Development of Mark V would require a continuous power supply with a high duty cycle current. The possibility to vary the power profile with variable inductors for current or frequency converters would assess plasma stability and electrode longevity. Higher feed rates should be tested, and an optimum for gas and carbon flow rates should be measured in order to determine the global maximum for each power setting. I would also recommend further *in situ* testing of the sublimator and optimization of sublimation conditions to ensure maximum extraction efficiency.

Another reactor parameter that was only briefly explored was the pressure during operation. As described in reference [40], the effect of pressure in arc processes had the greatest effect on yield, such that at a pressure of ~1/8 bar, there were 3-4 times increase in extractable yield. If this effect was translated to our atmospheric results, yields over 20% are possible. The impact on profitability is immediate as analyzed in the sensitivity analysis [Section 14.2.4].

Once the variables are tested and optimized, I would recommend a detailed economic analysis before it is scaled up to an industrial scale.

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Appendices

17 Appendix A: Fullerene production processes

This appendix is a systematic literature review of fullerene synthesis methods.

17.1 Electric arc discharge

Haufler R.E., Chai, Y., Chibante L.P.F, Conceicao J., Jin C., Wang L., Maruyama S., Smalley R.E., "Carbon arc generation of C60", Material Research Society Symposium Proc. Vol. 206 1991 [40]

One of the first methods to produce fullerenes on the macro scale. Fullerenes were made available as a solid for scientists to study. Fullerene yields as high as 15% were reported and fullerene formation in different environments was tested. The need for a buffer gas to ensure fullerene production was explored. Helium as the buffer gas was determined to have the highest yields.

Reactor Volume & MOC: 25cm^3 stainless steel and 0.063 L tubular graphite

Carbon Source: Graphite Electrodes

Process: Batch

Power: 150 Amps DC

Yield: 3-15%

Gas: Helium/Argon

Reactor Pressure: 100-200 torr

Purification: not stated

Sesli A., Cicek B. and Oymael M., "Fullerene Production in a Graphite Tubular Reactor" Fullerenes, Nanotubes, and Carbon Nanostructures, 12:1-11, 2005 [73]

Fullerene synthesis using the electric arc discharge technique is presented.

The authors test fullerene production in a tubular reactor to determine the effects of helium flow on the production of fullerene. Two reactor volumes were also tested, the first one being a 5-litre stainless steel reactor which provided a maximum yield of 16.2% and the second one being a graphite tubular reactor with fullerene yields as high as 32% if there was continuous helium flow on one end and steady suction on the other. Yields of ~1% were obtained for static helium (no flow) keeping the remaining conditions constant.

The main drawback of the system was the formation of cathodic deposits which limited the maximum runtime to under 10 minutes as it would inhibit erosion. The cathode which is the graphitic tubular reactor needs replacement, and the current soot production rates are extremely low even when compared to other arc discharge processes.

Reactor Vol. & MOC: 5-L stainless steel and 2 cm diameter, 20 cm length tubular graphite

Carbon Source: Graphite Electrodes

Process: Batch

Power: 45-100 Amps DC

Yield: 1-32%

Gas: Helium

Reactor Pressure: 100 torr

Kyesmen P., Onoja A., Amah A., "Fullerenes synthesis by combined resistive heating and arc discharge techniques". Springer Plus (2016) 5:1323 [74]

The production of fullerenes using arc discharge and resistive heating is reported. The researchers were able to obtain yields of 6% fullerenes; however, the soot production was limited (43.67 mg) as the maximum run time was 2mins. The use of resistive heating along with arc discharge helped improve overall soot production to 110 mg; however, the yield dropped to 4%.

Reactor Volume & MOC: Not stated and stainless steel

Carbon Source: Graphite Electrodes

Process: Batch

Power: 150 Amps DC

Yield: 6%

Gas: Helium

Reactor Pressure: 200 torr

Purification: Dissolved in Boiling Toluene. Recrystallization by concentration followed by using diethyl ether to wash for hydrocarbons

Kyesmen P.I., Onoja A.D., Amah A.N. "Fullerene synthesis using fabricated arc discharge system with relatively large chamber size". J. of Applied Physics Vol.7, 2015, issue 6, pp 77-83 [75]

The paper describes the use of electric arc discharge at two sub-atmospheric pressures in a relatively large chamber (120 mm diameter, 500 mm length) to produce fullerenes. The author's premise of increase in chamber size would help reduce pressure change effects when the arc discharge is in use seems to hold as they obtained a yield of 6-8% in comparison to 3-4% obtained from a smaller chamber (100 mm diameter and 200 mm length) keeping all other conditions constant. The researchers also obtained better yields at lower pressure, 100 torr in comparison to 200 torr.

The system used graphite electrodes as the source of carbon for production thereby requiring a consumable moving electrode which makes it a batch process. The system can be only run for 2 mins, and max soot yield was only ~44 mg.

Reactor Volume/dimensions & MOC: 120 mm diameter, 500mm length and S.S

Carbon Source: Graphite Electrodes

Process: Batch

Power: 100-150 Amps DC

Yield: 6-8%

Gas: Helium

Reactor Pressure: 100-200torr

Purification: Dissolved in boiling toluene; recrystallization by concentration followed by using diethyl ether to wash for hydrocarbons

17.2 Laser synthesis

Armand X, Herlin N, Voicu I, Cauchetier M. "Fullerene synthesis by laser pyrolysis of hydrocarbons". J Phys. Chem. Solids Vol. 58, no 11. Pp 1853-1859,1997 [76]

A new method for fullerene production using laser was investigated. Various hydrocarbons such as ethylene, acetylene, and benzene were used as the carbon source in the aerosol form. A high-power CO_2 laser was used as the heating source. Sulfur hexafluoride is used as a sensitizer as acetylene and benzene are transparent to the CO_2 laser.

Sooting was attempted with both focused and unfocused beam and fullerenes were detected only when the beam was focused. High temperature, low pressure, and hydrogen scavenger were determined to be essential for fullerene formation.

Weighable quantities of fullerenes (5-20 mg/hr) were produced; however, the max yield was only 1%. There is a possibility for improvement of the process with higher laser power, different wavelength or different precursors.

Laser: CO2 laser, CILAS CI 1000 & PRC-Oerlikon 1500, 10.6 um

Reactor MOC: Glass

Carbon Source: Ethylene, acetylene, and benzene

Pressure- 166-760 torr

Yield: 0.02-1%

Purification: Heated toluene Soxhlet followed by ether wash and drying

Oyama T., Ishii T., Takeuchi K. "Synthesis of fullerenes by ablation using pulsed and cw-Nd: YAG lasers". Fullerene Science and Technology, 5(5), 919-933, 1997 [77]

Macroscopic production of fullerenes by laser ablation of graphite in an inert environment was investigated.

Fullerene production was achieved only when the target temperature was above 700 °C after which it increased linearly up to 2300 °C.

The pressure seemed to have a profound effect on fullerene yield. A bell curve was observed with the fullerene yields decreasing significantly below 20 kPa and above 107 kPa. The low pressure allowed carbon vapors to diffuse further away leading to lesser collisions and decreased yield while at high pressure the carbon vapor coalesces and cool down quickly which results in lower yields. Optimal pressure was determined to be between 53kpa and 80kpa.

Unlike the arc discharge method, fullerene yields seem to drop when using helium as buffer gas in laser ablation.

The main advantage of this method is the high production of C_{70} (34-31%) in comparison to the contact arc method (10-15%) of the fullerenes collected.

Reactor Spec: 40 mm id quartz tube, 6 mm diameter graphite rod

Laser: cw-Nd: YAG laser (NEC SL116D) and Q-Switched pulsed (10nS) Nd: YAG laser (Continuum Powerlite 9010)

Gas: 0.5 slpm of argon

Purification: submerge quartz tube in toluene, sonication followed by filtration.

Yield: 0.05-0.8 mg/hr

Kasuya D., Kokai F., Takahashi K., Yudasaka M., Iijima S." Formation of C60 using CO2 laser vaporization of graphite at room temperature", Chemical Physics Letters 337 (2001) 25-30 [78]

C_{60} production at room temperature using a 500 ms pulsed CO_2 laser was reported. The highest yield was reported in helium at 150 torr, and it decreased with increase in pressure. The use of argon and nitrogen also reported decreased yields.

Fullerene is believed to be formed inside the plume as we know it requires high temperatures. The plume temperature was determined to be 3200-3300 °C, and as the plume is sufficiently long, it provides enough residence time for the carbon atoms to collide and form fullerenes.

Reactor Spec: Plastic resin chamber of 30x30x25 cm2 with a cylindrical graphite rod (50mm long, 30 mm od)

Gas: $He/Ar/N_2$

Pressure:150-760 torr

Laser: CO_2 laser (10.6 um, ~20 kW/cm^2, pulse width 500 ms)

Yield: 0.1-4% of collected

Purification: Dissolved in toluene

17.3 Solar synthesis

Flamant G., Robert J., Marty S., Gineste J., Giral J., Rivoire B., Laplaze D., "Solar Reactor Scaling up: the fullerene synthesis case study", Energy 29 (2004) 801-809 [79]

The authors run multiple experiments on a solar reactor at the 50 kW scale and use the data to calculate and design a 1 MW reactor. A max yield of 5% fullerene was obtained at an evaporation rate of 14.4 g/hr. It was also determined that increasing the target diameter beyond 30 cm resulted in a surface temperature drop below 3000 K because of which yields would drop as the vapor concentration would drop. A 22 cm outer diameter cylindrical target with a soot production rate between 80-150 g/hr (+19/-22%) would be achievable using a 1 MW solar reactor with a max yield of about 5%.

Solar Density: 7-8 kW/m^2

Solar Power: 50 kW

Soot production: 3.6-14.4 g/hr

Max Fullerene Yield: 5%

Chibante LPF, Thess A, Alford J.M., Diener M.D., Smalley R.E., "Solar Generation of Fullerenes", Journal of Physical Chemistry, Vol 97, No 34, 1993,8696-8700 [80]

The researchers used parabolic mirrors to collect sunlight onto a ¼ inch graphite target in sealed Pyrex tube with preheaters. The reaction took place at 50 torr under argon and was run for 3 hours as a proof of concept. 5 mg of soot was collected over the time frame and showed the presence of C_{60}. The small size of the apparatus was not enough to determine the feasibility of solar generation of fullerenes as the carbon vapor seemed to cool down way too quickly for fullerene formation and annealing.

Yield: trace quantities

Soot Production: 1.6 mg/hr

Solar radiation: solar radiation at 900 W/m^2 was focused down using parabolic mirrors

Fields C.L, Pitts J.R., Hale M.J., Bingham C., Lewandowski A., King D.E., "Formation of Fullerenes in Highly Concentrated Solar Flux", Journal of Physical Chemistry, 1993, 97, 8701-8702 [81]

An impressive design for a horizontal off-axis solar concentrator was presented. High solar concentrations of up to 2000 W/cm^2 were possible. The author's graphite cylinder 10mm in o.d and 6.3 mm in length as the target. Experiments ran for 30 seconds at a time at 50 torr pressures of either argon or helium. C_{60} and C_{70} were detected using a mass spec and HPLC; however, the yield has not been reported.

Solar density- 2000 W/m^2

Yield: Not determined

Soot Production: Not Reported

17.4 Combustion

Goel A, Hebgen P, Vander Sande J, Howard J, "Combustion synthesis of fullerenes and fullerenic nanostructures", Carbon 40, (2002) 177-182. [82]

Results show that fullerene formation is sensitive to changes in operating conditions, such as fuel/oxygen ratio, chamber pressure and the introduction of inert dilution gas. Fullerenic carbon and amorphous carbon is formed early in the flame, and with the increase in residence time in the flame the curvature of the structures seemed to improve. Largest fullerene yields in pre-mixed flame studies were found at low fuel to oxygen ratios; however, these are not ideal sooting conditions and provide only 2-3% soot formation efficiencies. Axial flame gas fullerene concentration analysis in a premised benzene/oxygen/argon flamed showed higher concentrations of fullerenes in the latter half of the flame away from the burner. Diffusion flame studies showed similar results as the premixed flame. The authors also tested other fuels such as naphthalene [83] , butadiene [83], toluene [84] and organics with halogen additives [85]. Of the pure fuels, it was determined that benzene produces the greatest amount of fullerenes [86] [83] [84].

They also concluded that lower pressure and higher temperatures resulted in higher fullerene concentrations.

Fuel: Benzene

Soot production at max yield: 2-3%

Yield: ~7%

Pressure: 20 torr

Takehara H, Fujiwara M, Arikawa M, Diener M, Alford J. M, "Experimental study of industrial-scale fullerene production by combustion synthesis", Carbon 43 (2005) 311-319. [87]

The researchers designed a unique premixed burner with ceramic insulation at the reaction zone to ensure a uniform high temperature. The system is set up to operate at 40 torr pressure with premixed toluene/oxygen as feedstock in a C/O ratio range of 0.99-1.28 for an experimental time of 6hrs. It was determined that the amount of fullerene in soot decreased with the increase in C/O ration; however, the amount of soot increased. The highest fullerene yield obtained was about 38%, but the total amount of soot collected was below 1%. An optimal of about 10% for both fullerene and soot production was achieved at a C/O ratio of about 1.2.

Pressure: 40 Torr

Fuel: Toluene/Oxygen

Optimal Fullerene Yield: ~10%

Optimal soot formation: ~10%

Alford JM., Bernal C, Cates M, Diener MD., "Fullerene production in sooting flames from 1,2,3,4-tetrahydronaphthalene", Carbon 46(2008) 1611-1625 [88]

Fullerene formation using a two-ring feedstock in opposed to the traditional one ring feedstock is compared. The authors run the apparatus at 40 torr pressure and between a C/O ratio of 1.04-1.19. Toluene was used as the one ring feedstock and provided yields between 1-1.25% for a sooting range of 4.5-7%. 1,2,3,4-Tetrahydronapthalene was used as the two-ring feedstock and gave a fullerene yield between 1.25-2.25% and sooting yields above that of toluene at all conditions between 4.5-8% thereby proving that two ring feedstocks would provide a better yield in combustion synthesis of fullerene in opposed to one ring feedstocks which are traditionally used.

Pressure: 40 torr

Fuel: 1,2,3,4- tetrahydronaphthalene/oxygen

Max soot formation: ~8%

Max Fullerene Yield: ~2.25%

Howard J, McKinnon T, Johnson E, Makarovsky Y, Lafleur A, "Production of C60 and C70 fullerenes in benzene oxygen flames", Journal of physical chemistry (1992), 96,6657-6662 [89]

The authors presented a unique design for the burner in which only the inner 70 mm of the burner plate was utilized for the experimental flame the annular 15 mm of the plate was used for a secondary non-sooting ethylene/argon/oxygen flame which is run fuel rich and is fed independently. This annular flame shields the experimental flame and allows the authors to approximate a one-dimensional core within which temperature and species concentration vary only with distance, or residence time from the burner surface thereby simplifying the analysis of data.

The research studied the dependence on temperature, pressure, C/O ratio and residence time of carbon in the flame. Best fullerene yield obtained was 0.26% with respect to the carbon fed in at 20 torr pressure. The highest production rate was achieved at 100 torr pressure with a C/O ratio of 0.76 and run times varied between 53-170 mins depending upon the conditions.

Yield: 0.26%

Soot formation: 0.0026-9.2%

Pressure: 100 torr

Fuel: Benzene

17.5 Plasma synthesis

Todorovic-Markovic B., Markovic Z., Mohai I., Karoly Z, Gal L., Foglein K., Szabo P.T., Szepvolgyi, "Efficient Synthesis of fullerenes in RF thermal plasma reactor", Chemical Physics Letters 378 (2003) 434-439 [37]

Fullerene production using a 27 kW RF plasma torch was studied. The apparatus was set up using a TEKNA PL-35 plasma torch powered by a generator operating between 3-5 MHz, the reactor is water cooled. Helium is used as plasma gas while argon was used as sheath gas. Graphite powder was injected from the top of the plasma flame with feed rates if 90-468 g/h. The main product, solid soot is collected from the reactor wall, and an HPLC analysis was conducted.

A yield of 4.1% was the best obtained at a graphite feed rate of 156 g/h.

Reactor Power: 27 kW

Yield: 4.1%

Feed rate: 156 g/h

Fullerene production rate: 6.5 g/hr

Carbon: graphite

Plasma type: RF plasma

Total gas flow rate: 55-67 slpm

Wang C., Imahori T., Tanaka Y., Sakuta T., Takikawa H., Matsuo H., "Synthesis of fullerenes from carbon powder by using high power induction plasma", Thin solid films 390 (2001) 31-36 [90]

The suitable experimental conditions adopted by the authors were 10-kPa plasma pressure, with a flow rate of 150 slpm for mixed-gas conditions of Ar, He and CO_2 with carbon powder as feedstock.

The plate power used is 30 kW along with a carbon feed rate of 5 g/min. Although yield was not quantified, C_{60} was detected when using helium or argon plasmas, the introduction of CO_2 made the fullerenes disappear.

Power: 30 kW

Flow Rate: 150 slpm

Feed rate- 5 g/hr

Yield: not determined

Carbon: Not mentioned < 20 um

Plasma type: RF Plasma

Chen Y, Zhang H, Zhu Y, Yu D, Tang Z, He Y, Wu C, Wang J, "A new method for fullerene production: pyrolysis of acetylene in high-frequency thermal plasma", Materials Science and Engineering 85 (2002) 29-32 [91]

The authors present a unique method to fullerene production using thermal plasma's, instead of using carbon black as a feedstock the authors use the torch for pyrolysis of acetylene to produce fullerenes. High flow rates of argon 10000 l/hr and 250l/hr of acetylene yields about 250 g/hr of soot. It is a simple process with low power requirements and might be a viable process for acetylene black plant to produce fullerene as a side product.

Power: 30 W

Total gas flow rate: 170 slpm

Feedstock: acetylene

Plasma: high frequency thermal

Soot flow rate: 250 g/hr

Fullerene production rate: 2.5 g/hr

Dubrovsky R., Bezmelnitsyn V., Eletskii A., "Plasma fullerene production from powdered carbon black", Carbon 42(2004) 1063-1066 [92]

A 12-kW commercial plasmatron, AP-3 from A-Flame Corporation was used for the study. The paper presented yields of up to 2% fullerene with respect to the carbon fed in.

The plasma stability seemed to decrease when the carbon feed rate is increased above 200 mg/minute. 1-3% of the Cu-Anode was detected in the collected soot by weight. It was also determined mathematically that complete vaporization of a 5um carbon black particle would be an order of magnitude quicker in helium than in argon.

Power: 12 kW DC

Total Gas flow rate: 18-20 slpm

Plasma: Plasmatron AP-3

Carbon feed rate: 200 mg/min

Fullerene yield: 2%

Carbon: 99.9% acetylene black

Fabry F, Fulcheri L. "Synthesis of carbon blacks and fullerenes from carbonaceous wastes by 3-phase AC thermal plasma". 6th International Conference on Engineering for Waste and Biomass vaporization, Waste Eng. May 2016, Albi, France. [93]

The paper presents a modified carbon black reactor to produce fullerenes using a high-temperature AC plasma in oppose to the DC ones used. AC power supplies are not only more efficient; they are also more economical. The authors run tests with N2 as plasma gas and carbon black as feedstock. The maximum yield obtained was 0.962% in the soot which is low; however, it is a good attempt at modifying an existing system for fullerene production.

The authors determined the low yields could be a result of impurities in the carbon and the fact that they were using nitrogen as a plasma gas reacts with carbon vapor to form CN which in turn reduced the number of carbon atoms available for fullerene formation. The system as it stands used high gas flow rates with low yields but has scope for improvement.

Plasma Power: 36 kW AC 3-phase (180 A, 150V)

Plasma Gas: N_2

Total Gas flow rate: 3470 slpm

Soot flow rate: 800 g/hr

Best Fullerene Yield: 0.962%

Fulcheri L., Schwob Y., Fabry F., Flamant G., Chibante LPF., Laplaze D., " Fullerene production in a 3-phase AC plasma process", Carbon 38 (2000) 797-803. [94]

The paper presents a fullerene reactor with a 100 kW 3phase AC plasma torch. They study 10 different grades of commercially available carbon as feedstock to determine the ideal feedstock for fullerene synthesis.

Fullerenes were only produced with 3 grades of acetylene black and one grade of synthetic graphite powder, no fullerenes were produced with cokes or carbon blacks. This shows a high sensitivity of impurities in carbon feedstock on the production of fullerenes.

Plasma power: 100 kW 3phase AC

Plasma gas flow rate: 30-80 slpm

Carbon feed rate: 0.5-1.5 kg/hr

Best Fullerene Yield in soot: 3.58%

Fulcheri L., Fabry F., Rohani V., "The influence of the carbon precursor, carbon feed rate and helium gas flow rate on the synthesis of fullerenes from carbon powder in an entrained flow 3-phase AC plasma reactor operating at atmospheric pressure", Carbon 50(2012) 4524-4533 [64]

The researchers optimize a 250 kVA AC plasma reactor and test different variable to determine the maximum yield and highest production rate possible. They test 4 different feedstocks varying in size, porosity, and purity. It was determined that the smallest particle size with high porosity and purity was the best feedstock. Acetylene black (Y50A) yielded the best results with a maximum yield of 4.5%. A production rate of 17 g/hr of fullerenes was achieved at a carbon feed rate of 480 g/hr and a yield of 3.6% with Y50A.

Plasma Power: 19 kW (220 A, 80 V)

Carbon Feed rate: 200-600 g/hr

Gas Flow rate: 166-580 slpm carrier gas + 3333 slpm for quench

Best Yield: 4.5%

18 Appendix B: Tekna nanopowder feeder calibration plot

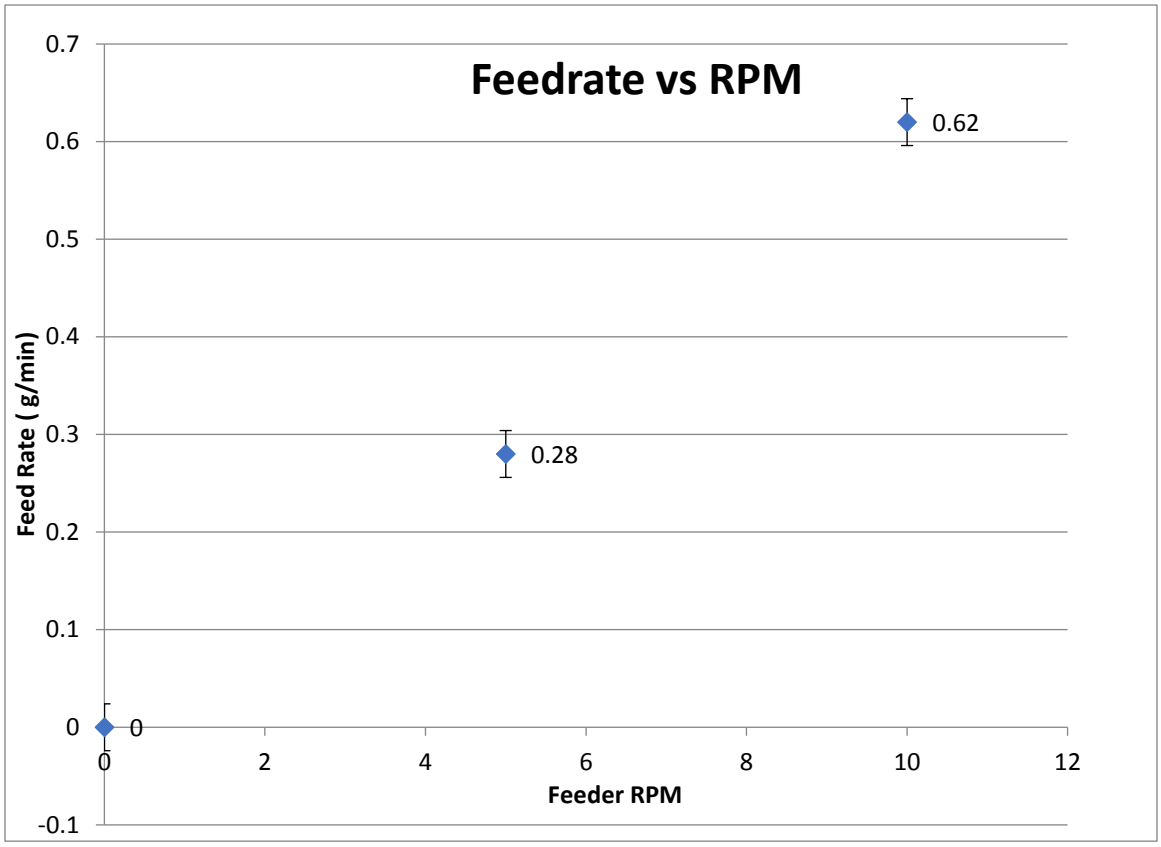
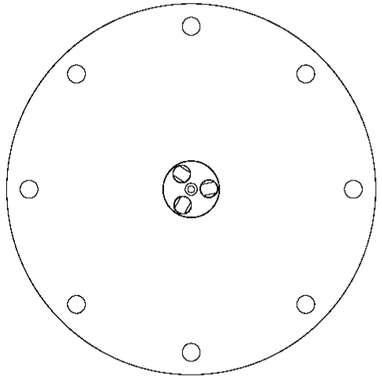
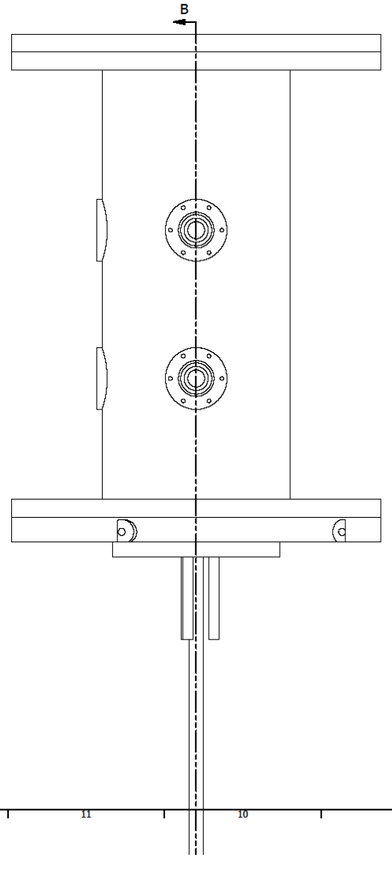


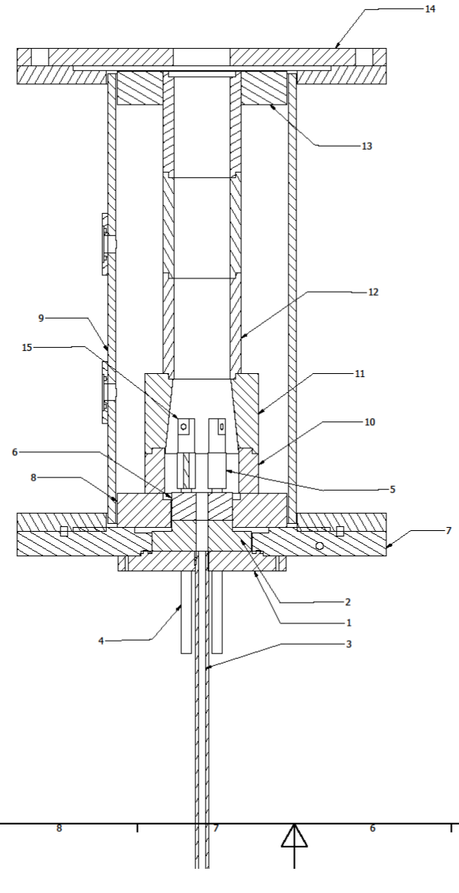
Figure 76: Feeder calibration

19 Appendix C: MARK IV Machine drawings





SECTION B-B
SCALE 1 / 2



PARTS LIST			
ITEM	QTY	PART NUMBER	DESCRIPTION
1	1	new torch design	G10 TO HOLD THE TORCH TOGETHER
2	1	G2.5_HS_V1_P1	TORCH HEAT SHIELD
3	1	Gen2.5. Mcr feeder rod threaded	MACOR/G10 FEED TUBE
4	3	G2.5_brass_p2_solid with threads_v3 shortened	BRASS ELECTRODES
5	3	G2.5_ADOP_V1	GRAPHITE ADAPTER
6	1	C60E3218 heat shield 3 part 2	TORCH HEAT SHIELD
7	1	C60A3205 water cooled flange gen2.5	BOTTOM SS FLANGE
8	1	G2.5_CERAMIC RING_REV1	BOTTOM CERAMIC RING
9	1	C60A3202	STEEL SHELL
10	1	gen3.1 bottom graphite chamber	FIRST GRAPHITE CHAMBER
11	1	gen 3.1 graphite chamber botton 2	GRAPHITE EXPANSION CHAMBER
12	3	gen 3.1 graphite common chamber	ALL OTHER GRAPHITE PIECES FOR SHELL
13	1	gen3.1 top ceramic ring	TOP HEAT SHIELD FROM CASTABLE CERAMIC
14	1	Circular Reactor Top Flange	TOP SS FLANGER
15	3	C60E3214	GRAPHITE HOLDER
16	3	ELECTRODE TIP	GRAPHITE NUBS

REV NO	REVISION NOTE	BY	DATE

MATERIALS

TOLERANCES mm UNLESS OTHERWISE SPECIFIED

MACHINED	FROM	0.5	3	6	30	120	400	
	UP TO	3	6	30	120	400	1000	
	±	0.1	0.1	0.2	0.3	0.5	0.8	
WELDED	FROM	2			30	120	400	
	UP TO	30			120	400	1000	
	±	1			2	2	3	

ANGLES ± 1 DEGREE SURFACE FINISH 3.2 um
BREAK ALL SHARP CORNERS
CHAMFER FIRST THREAD ON TAPPED HOLES

DRAWN		11/15/2018
CHECKED		
QA		
MFG		
APPROVED		

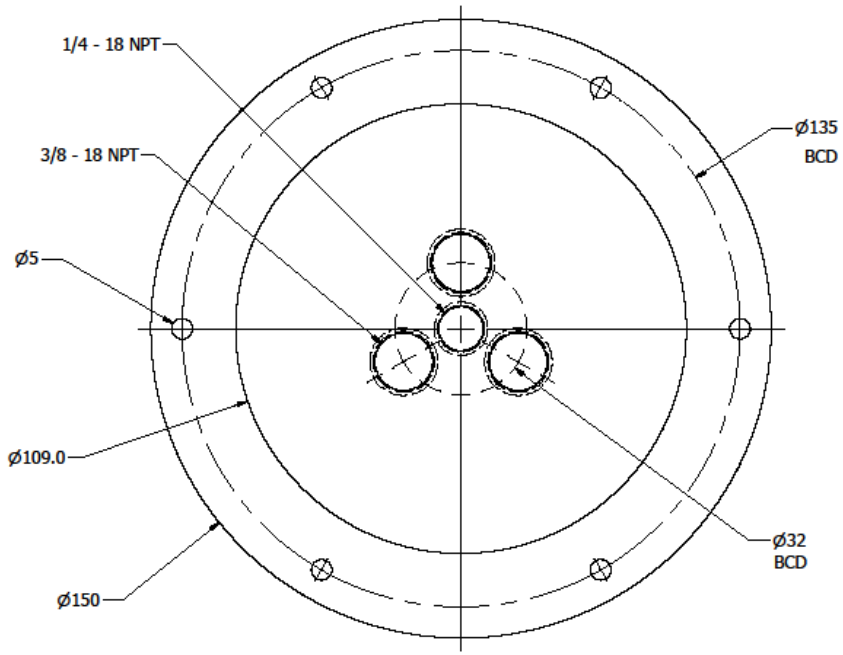
AIF FULLERENE REACTOR

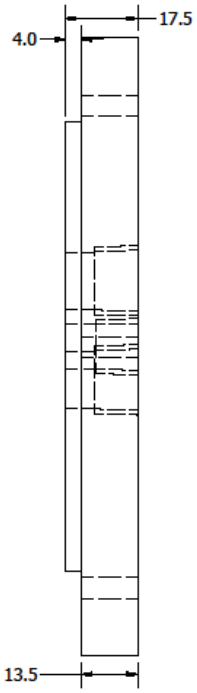
TITLE: MARK IV ASSEMBLY

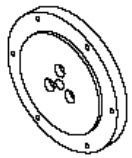
SIZE A1 | DWG NO MARK IV ASSEMBLY | REV

SCALE 1/2 | SHEET 1 OF 1

PRODUCED BY AN AUTODESK EDUCATIONAL PRODUCT







REV NO	REVISION NOTE	BY	DATE
0	ISSUE FOR CONSTRUCT	AS	04/12/2016
A	EDIT FOR SEALING	EF	05/04/2016
	issued for construction		dec 8 2016

MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asairawag	4/12/2016
SUPPLIED G10	MACHINED FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; +- 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
	WELDED FROM 2 30 120 400 / UP TO 30 120 400 1000; +- 1 2 2 3	QA	
	ANGLES +- 1 DEGREE SURFACE FINISH 3.2 um	MFG	
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES	APPROVED	

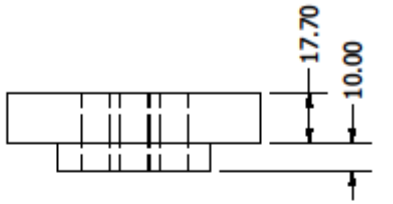
UNB FULLERENE REACTOR

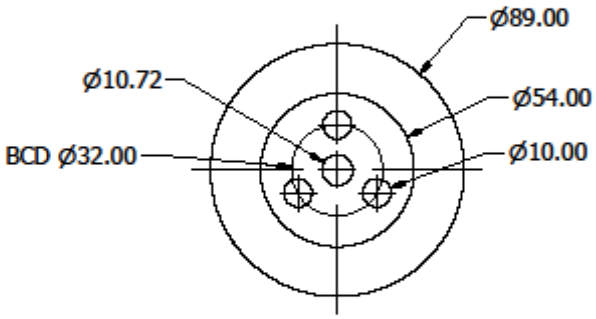
TITLE: ELECTRODE TORCH ASSEMBLY

SIZE B | DWG NO E3220 | REV

SCALE 1:1 | SHEET 1 OF 1

PRODUCED BY AN AUTODESK EDUCATIONAL PRODUCT





REV NO	REVISION NOTE	BY	DATE
O	ISSUE TO CONSTRUCT	AS	

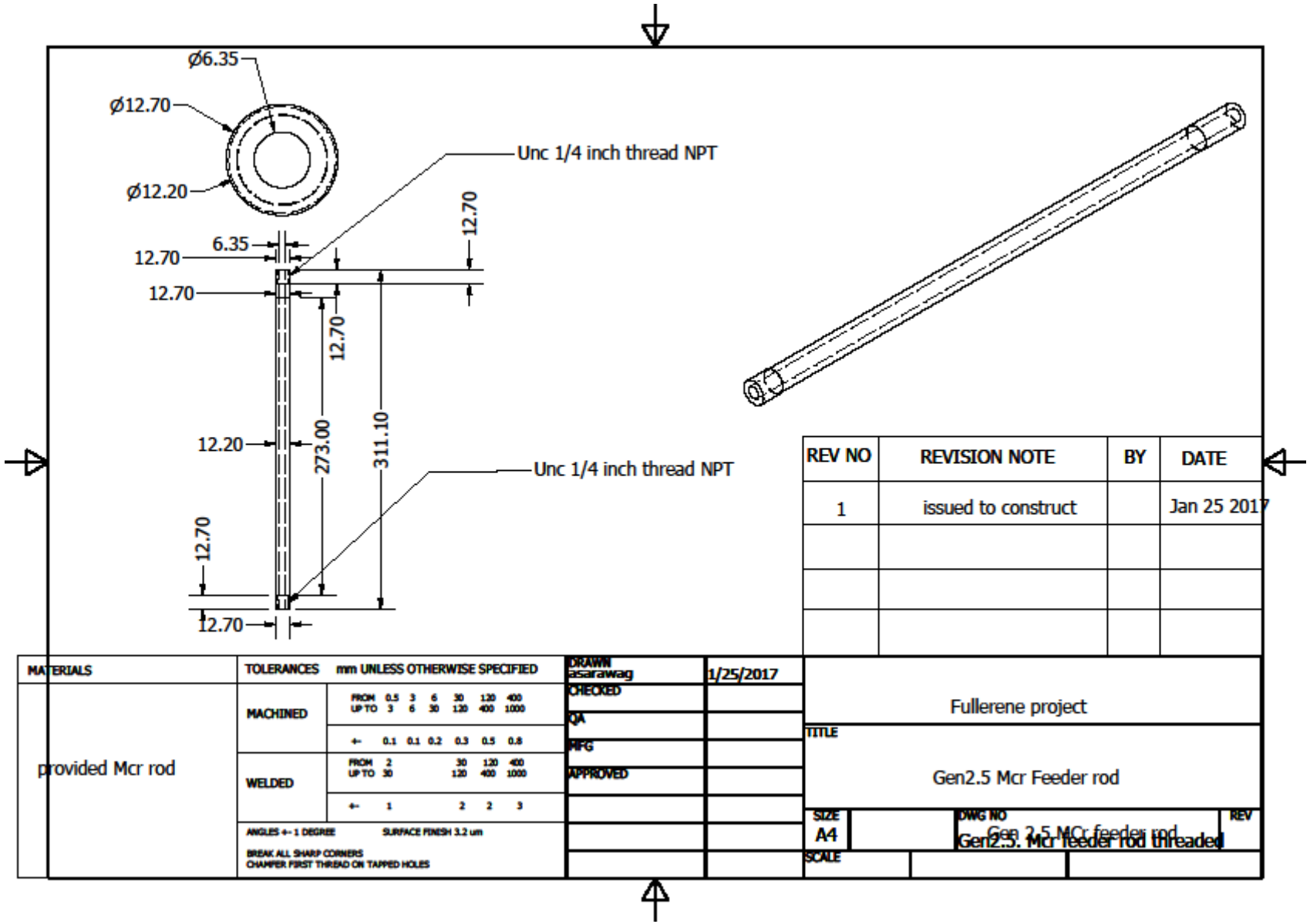
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	11/15/2018
SUPPLIED FIRE BRICK	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ± 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
		QA	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ± 1 2 2 3	MFG	
		APPROVED	
	ANGLES ± 1 DEGREE SURFACE FINISH 3.2 um		
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES		

AIF FULLERENE REACTOR

TITLE: HEAT SHIELD

SIZE	DWG NO	REV
A4	G2.5_HS_V1_P1	

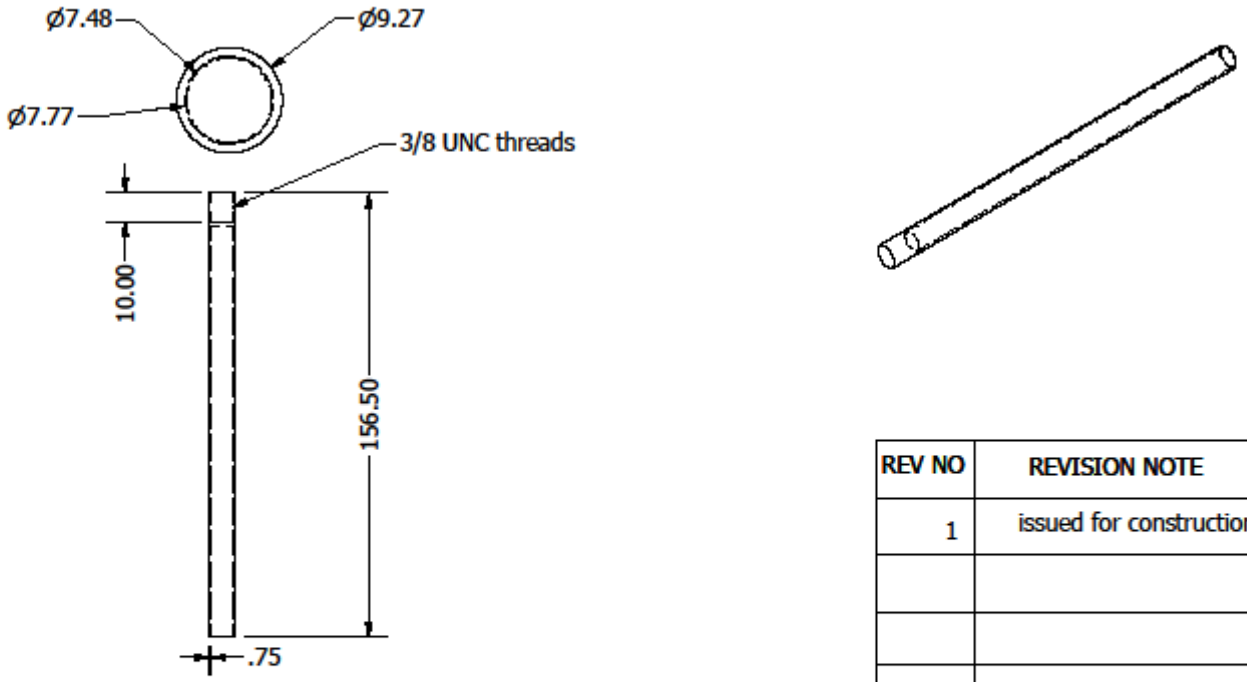
SCALE 1/2 SHEET 1 OF 1



REV NO	REVISION NOTE	BY	DATE
1	issued to construct		Jan 25 2017

MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	1/25/2017
provided Mcr rod	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
		QA	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	MFG	
		APPROVED	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um		
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES		

Fullerene project		
TITLE: Gen2.5 Mcr Feeder rod		
SIZE A4	DWG NO Gen 2.5 MCr feeder rod Gen2.5. Mcr feeder rod threaded	REV
SCALE		



REV NO	REVISION NOTE	BY	DATE
1	issued for construction		Dec 15 2016

MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	12/15/2016
Solid brass rod	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
		QA	
		MFG	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	APPROVED	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um		
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES		

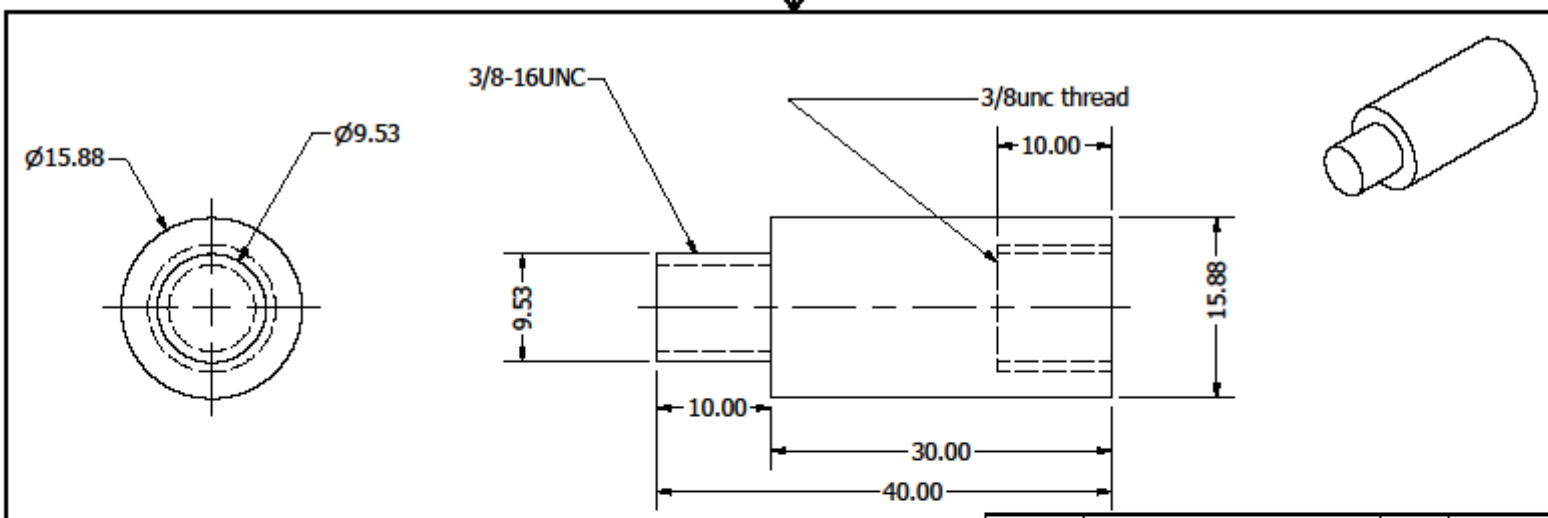
AIF fullerene project

TITLE: solid brass electrode

SIZE A4 | DWG NO G2.5_brass_p2_solid with threads_v3-1 | REV

SCALE

SHEET 1 OF 1



REV NO	REVISION NOTE	BY	DATE
O	ISSUE TO CONSTRUCT	EF	Dec 15 2016

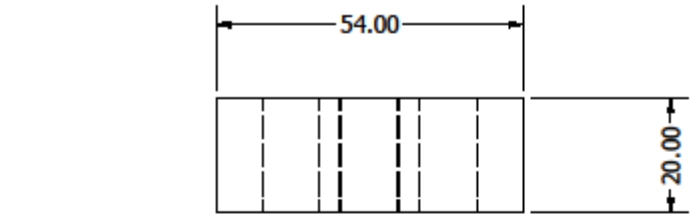
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN adevaris	6/30/2016
SUPPLIED GRAPHITE	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
		QA	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	MFG	
		APPROVED	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um		
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES		

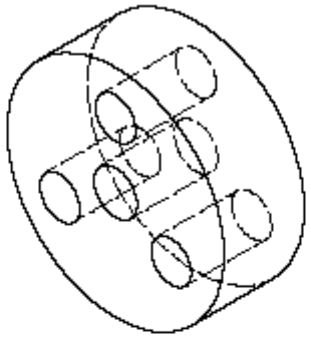
AIF FULLERENE REACTOR

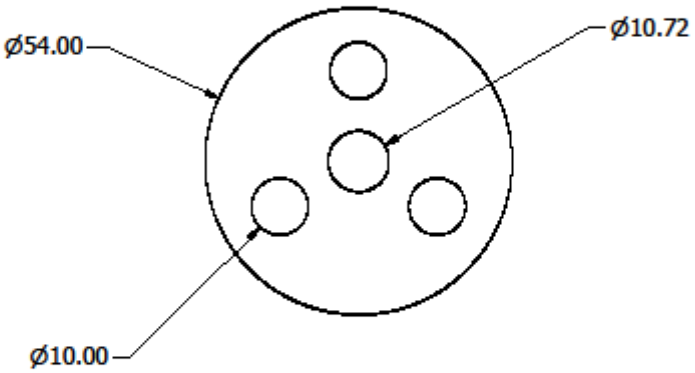
TITLE: ELECTRODE ADAPTER

SIZE	DWG NO	REV
A4	G2.5_ADOP_V1	

SCALE 2:1 SHEET 1 OF 1







REV NO	REVISION NOTE	BY	DATE
1	Issue to Construct	AS	Feb 15,2017

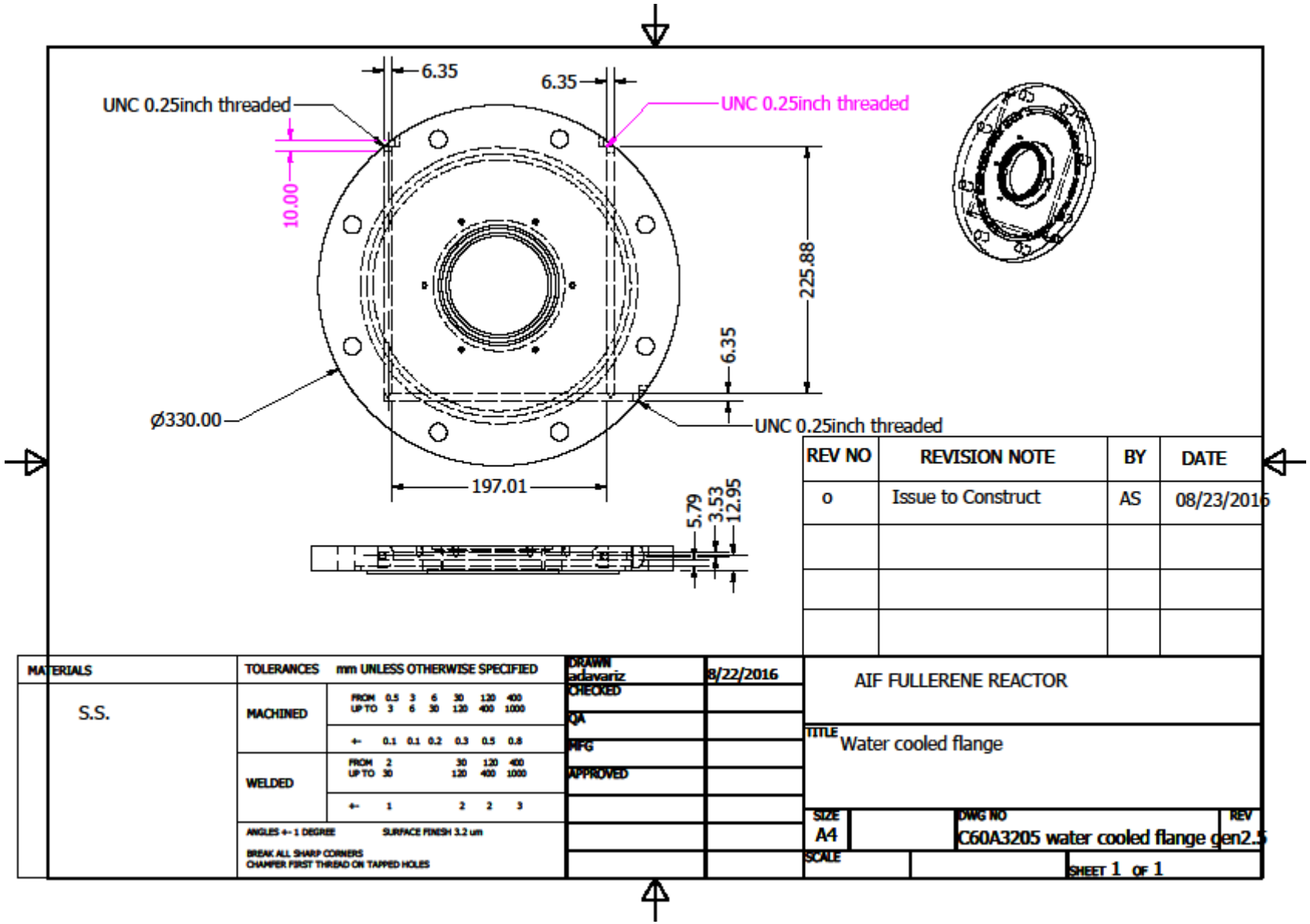
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	2/15/2017
Provided fire brick	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	QA	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um	MFG	
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES	APPROVED	

AIF FULLERENE REACTOR

TITLE: Heat shield top part

SIZE: A4 | DWG NO: C60E3218 heat shield 3 part 2 | REV:

SCALE:



REV NO	REVISION NOTE	BY	DATE
0	Issue to Construct	AS	08/23/2016

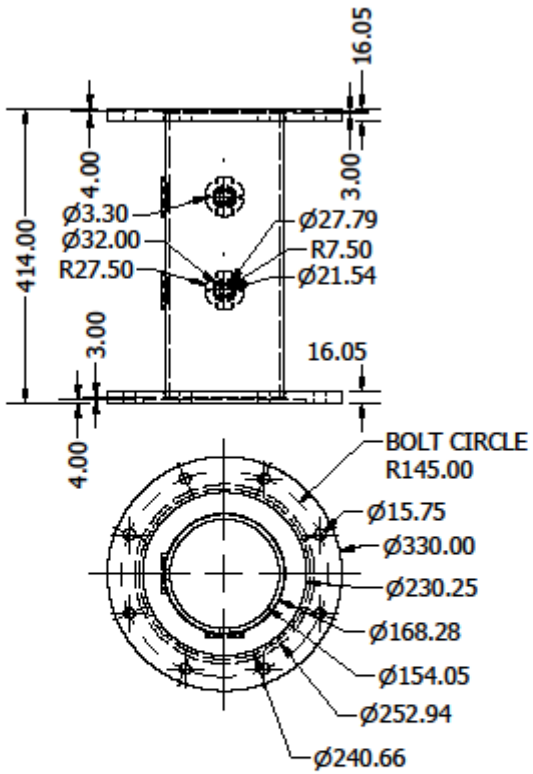
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN adavariz	8/22/2016
S.S.	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
		QA	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	MFG	
		APPROVED	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um		
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES		

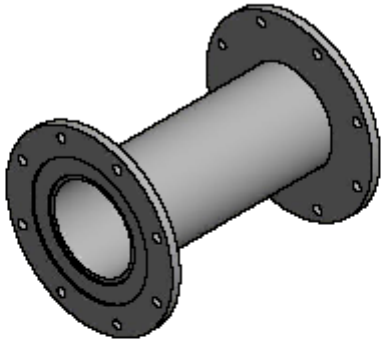
AIF FULLERENE REACTOR

TITLE: Water cooled flange

SIZE A4 | DWG NO C60A3205 water cooled flange gen2.5 | REV

SCALE | SHEET 1 OF 1





REV NO	REVISION NOTE	BY	DATE
0	ISSUE TO CONSTRUCT	AS	

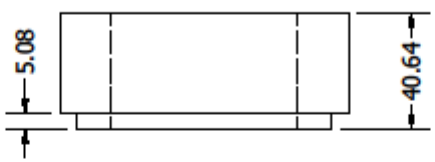
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	11/15/2018
SUPPLIED STEEL	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	QA	
		MFG	
		APPROVED	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um		
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES		

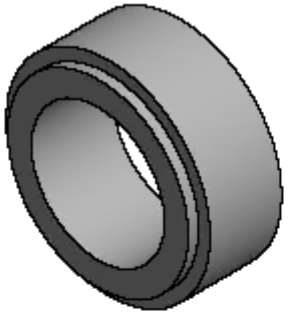
AIF FULLERENE REACTOR

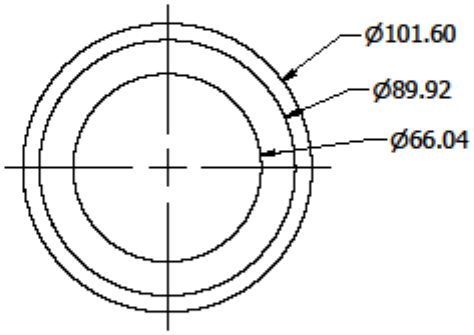
TITLE: STEEL CHAMBER

SIZE	DWG NO	REV
A4	C60A3202	

SCALE 1/8 SHEET 1 OF 1







REV NO	REVISION NOTE	BY	DATE
O	ISSUE TO CONSTRUCT	AS	

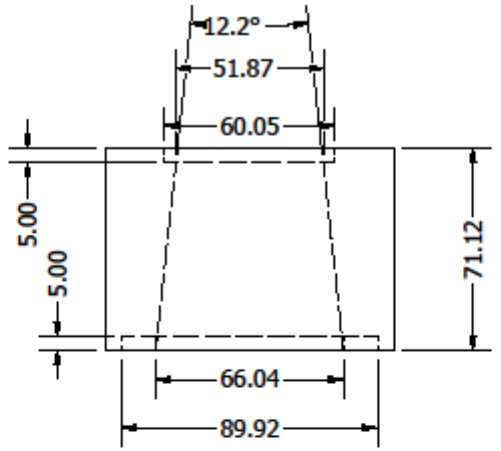
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	11/15/2018
SUPPLIED GRAPHITE	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	QA	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um	MFG	
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES	APPROVED	

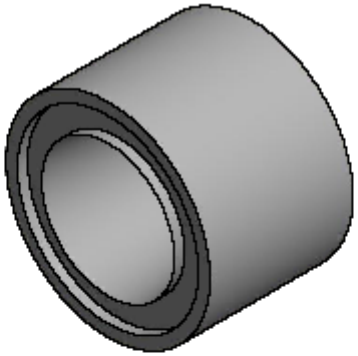
AIF FULLERENE REACTOR

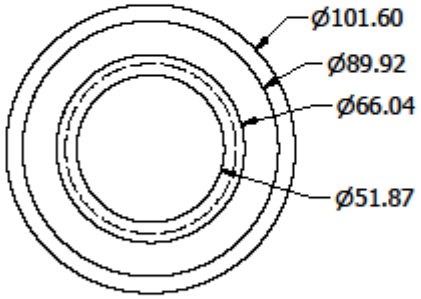
TITLE: BOTTOM GRAPHITE CHAMBER

SIZE A4 | DWG NO gen3.1 bottom graphite chamber | REV

SCALE 1/2 | SHEET 1 OF 1







REV NO	REVISION NOTE	BY	DATE
O	Issue to Construct	AS	Jan 2018

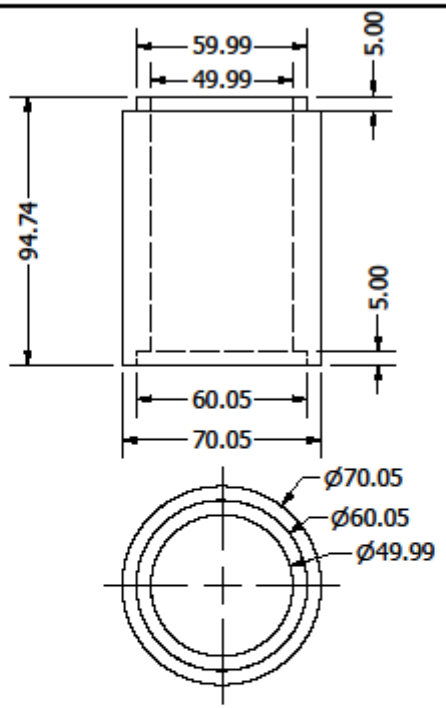
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	11/15/2018
Supplied Graphite	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	QA	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um	MFG	
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES	APPROVED	

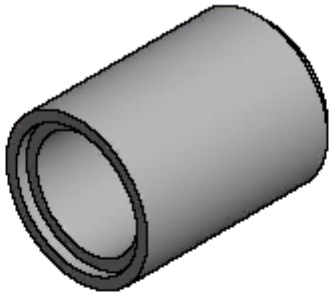
AIF FULLERENE PROJECT

TITLE: GRAPHITE EXPANSION CHAMBER

SIZE A4 | DWG NO gen 3.1 graphite chamber botton 2 | REV

SCALE 1/2 | SHEET 1 OF 1





REV NO	REVISION NOTE	BY	DATE
O	ISSUE TO CONSTRUCT	AS	JAN 2018

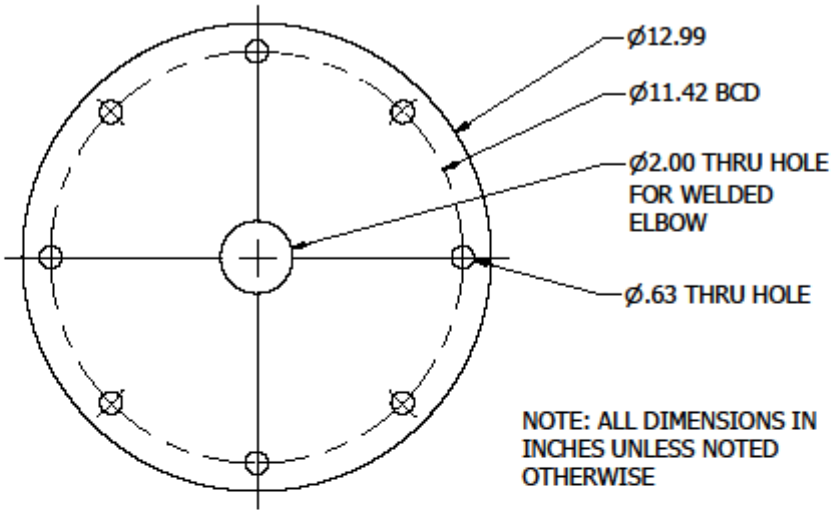
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	11/15/2018
Supplied Graphite	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	QA	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um	MFG	
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES	APPROVED	

AIF FULLERENE REACTOR

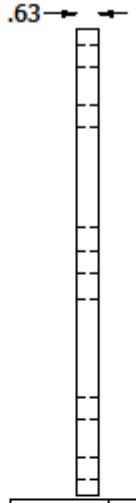
TITLE: GRAPHITE CHAMBER

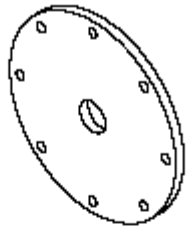
SIZE	DWG NO	REV
A4	gen 3.1 graphite common chamber	

SCALE 1/2 SHEET 1 OF 1



NOTE: ALL DIMENSIONS IN INCHES UNLESS NOTED OTHERWISE

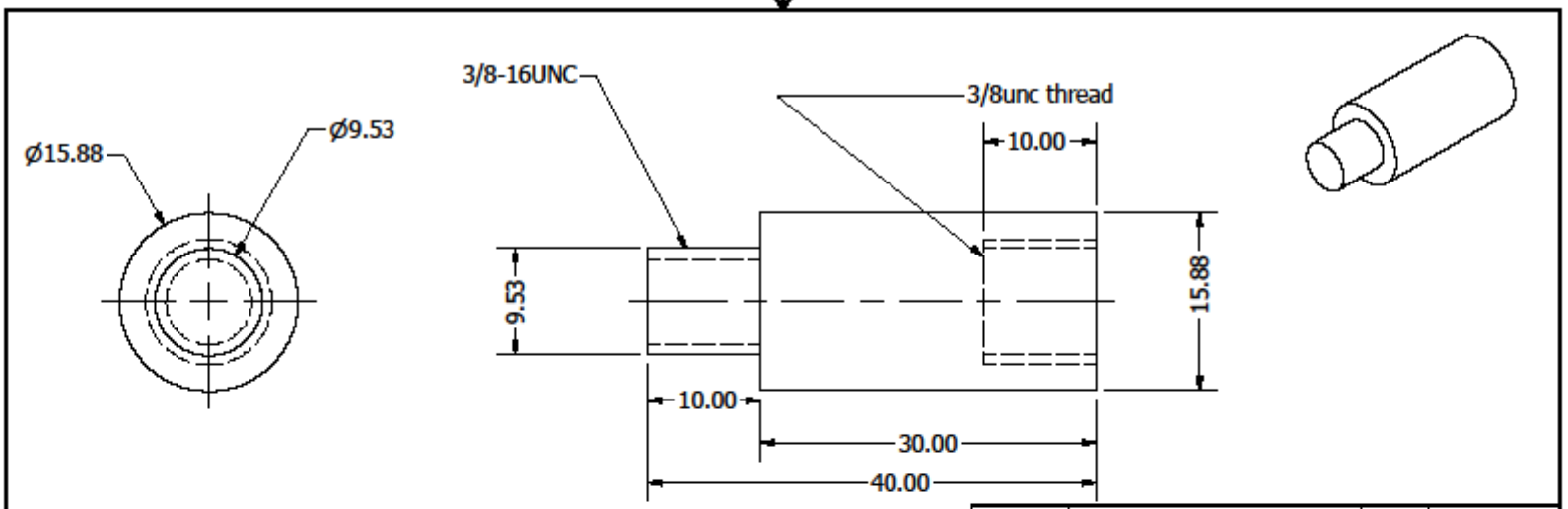




REV NO	REVISION NOTE	BY	DATE
OS	ISSUE TO CONSTRUCT	EF	09/06/17

MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN asarawag	9/6/2017
SUPPLIED STEEL	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	QA	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um	MFG	
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES	APPROVED	

AIF FULLERENE REACTOR GEN 3.0			
TITLE: TOP FLANGE FOR REACTOR			
SIZE A4		DWG NO Circular Reactor Top Flange 3.0	REV
SCALE 1/4			



REV NO	REVISION NOTE	BY	DATE
O	ISSUE TO CONSTRUCT	EF	Dec 15 2016

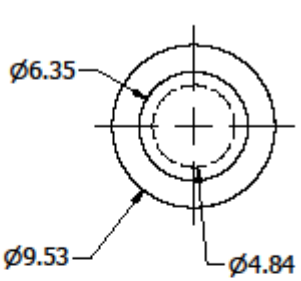
MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED	DRAWN adevaris	6/30/2016
SUPPLIED GRAPHITE	MACHINED: FROM 0.5 3 6 30 120 400 / UP TO 3 6 30 120 400 1000; ← 0.1 0.1 0.2 0.3 0.5 0.8	CHECKED	
		QA	
	WELDED: FROM 2 30 120 400 / UP TO 30 120 400 1000; ← 1 2 2 3	MFG	
		APPROVED	
	ANGLES ← 1 DEGREE SURFACE FINISH 3.2 um		
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES		

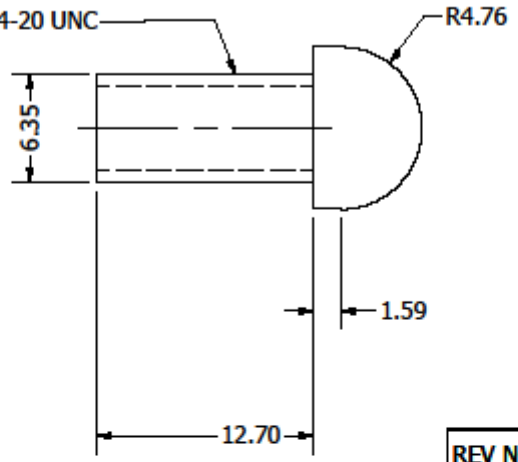
AIF FULLERENE REACTOR

TITLE: ELECTRODE ADAPTER

SIZE	DWG NO	REV
A4	G2.5_ADOP_V1	

SCALE 2:1 SHEET 1 OF 1





NOTE: ALL DIMENSIONS ARE IN MM UNLESS OTHERWISE SPECIFIED

REV NO	REVISION NOTE	BY	DATE
O	ISSUED TO CONSTRUCT	AD	06/22/16

MATERIALS	TOLERANCES mm UNLESS OTHERWISE SPECIFIED								
SUPPLIED GRAPHITE	MACHINED	FROM / UP TO	0.5 3	3 6	6 30	30 120	120 400	400 1000	
		±	0.1	0.1	0.2	0.3	0.5	0.8	
	WELDED	FROM / UP TO	2 30			30 120	120 400	400 1000	
		±	1			2	2	3	
	ANGLES ± 1 DEGREE SURFACE FINISH 3.2 um								
	BREAK ALL SHARP CORNERS CHAMFER FIRST THREAD ON TAPPED HOLES								

DRAWN adevaris	6/22/2016	AIF FULLERENE REACTOR
CHECKED		TITLE: ELECTRODE TIP V3
QA		
MFG		
APPROVED		
		SIZE A4 / DWG NO G3_ElecTip_v2 / REV
		SCALE 3:1 / SHEET 1 OF 1

20 Appendix D : Economic analysis

20.1 Installation costs

Installation Costs	Equipment Cost	Installation Cost
Tekna Nanopowder Feeder PFR400	25000	1716
Tekna Nanopowder Feeder PFR400	25000	1716
Reactor	50000	18760
3-zone electric furnace for sublimation	20000	1166
Pulse-jet candle filter for soot separation	44000	19800
Pulse-jet candle filter for fullerite separation	44000	19800
3 phase AC plasma power supply	26000	132
water chiller	11000	208
Soot storage tank	3100	1395
Fullerite storage tank	3100	1395

20.2 Working capital

Material	Quantity	Unit	Cost/Unit	Total
Helium	864	m3	10	9120
Carbon	9	kg	15.5	140

20.3 Maintenance costs

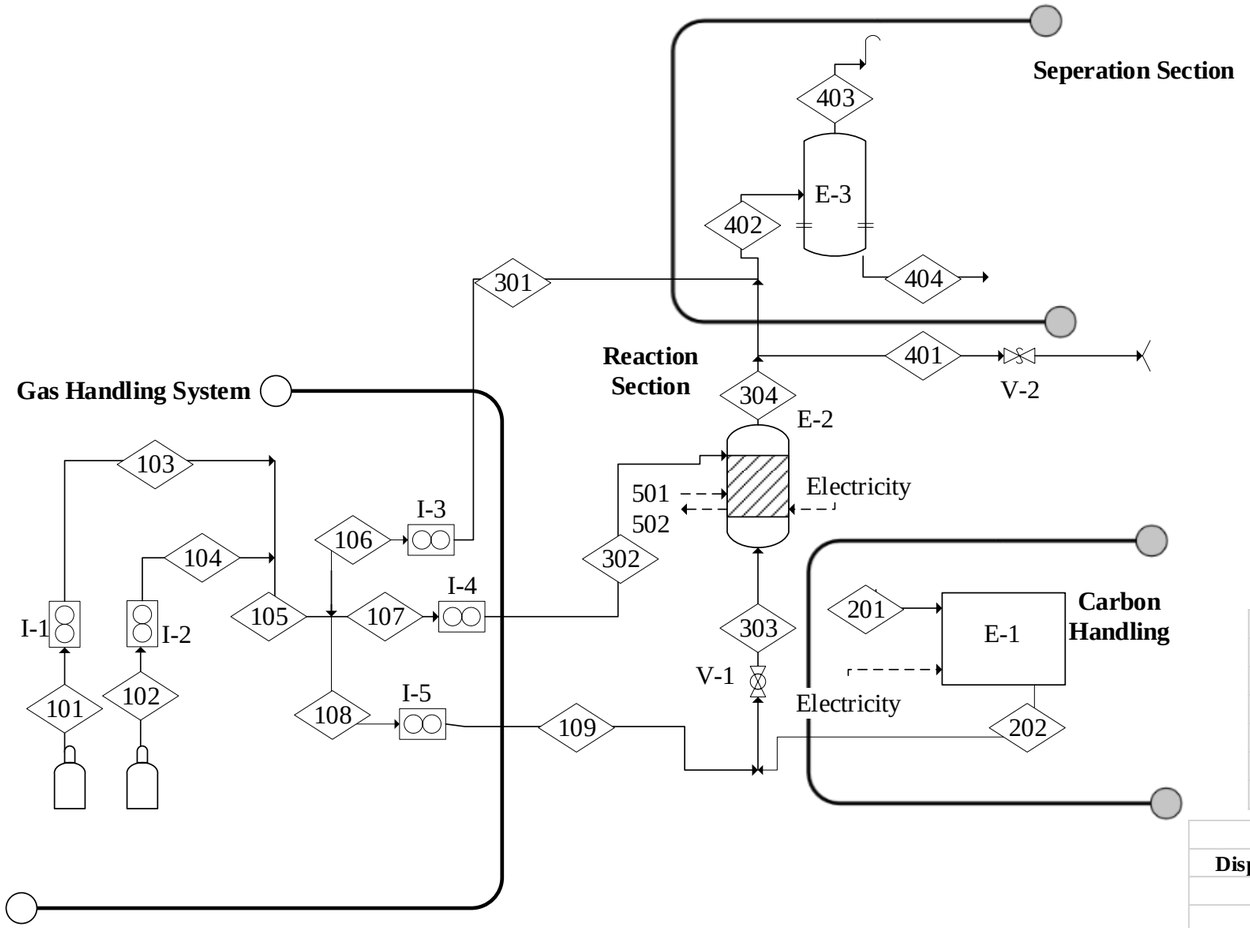
Maintenance	Cost
Graphite	15000
Power supply	9000
Engineering services	15000
Office Supplied	1000
Total	**39000**

20.4 Labor benefits

Additional Labor Cost /year		
Vacation	2912	2 weeks paid
Paid Holidays overtime	2808	9 total
EI	1205	for above 51300/year or 1.62%*1.4
CPP	2750	5.09% up to 54000, 2750 max
Total / op	9675	
no. of op	10	
Total operators	96750	
Supervisor		
Vacation	3774.4	2 weeks paid
Paid Holidays overtime	3639.6	9 total
EI	1205	for above 51300/year or 1.62%*1.4
CPP	2750	5.09% up to 54000, 2750 max
Total /sup	11369	
Machinist		
Vacation	2240	1 week paid
Paid Holidays overtime	2160	9 total .5 paid days
EI	825.552	for above 51300/year or 1.62%*1.4
CPP	1852.76	5.09% up to 54000, 2750 max
Total /sup	7078.312	

21 Appendix E: Process Flow Diagrams

MARK IV Process Flow Diagram

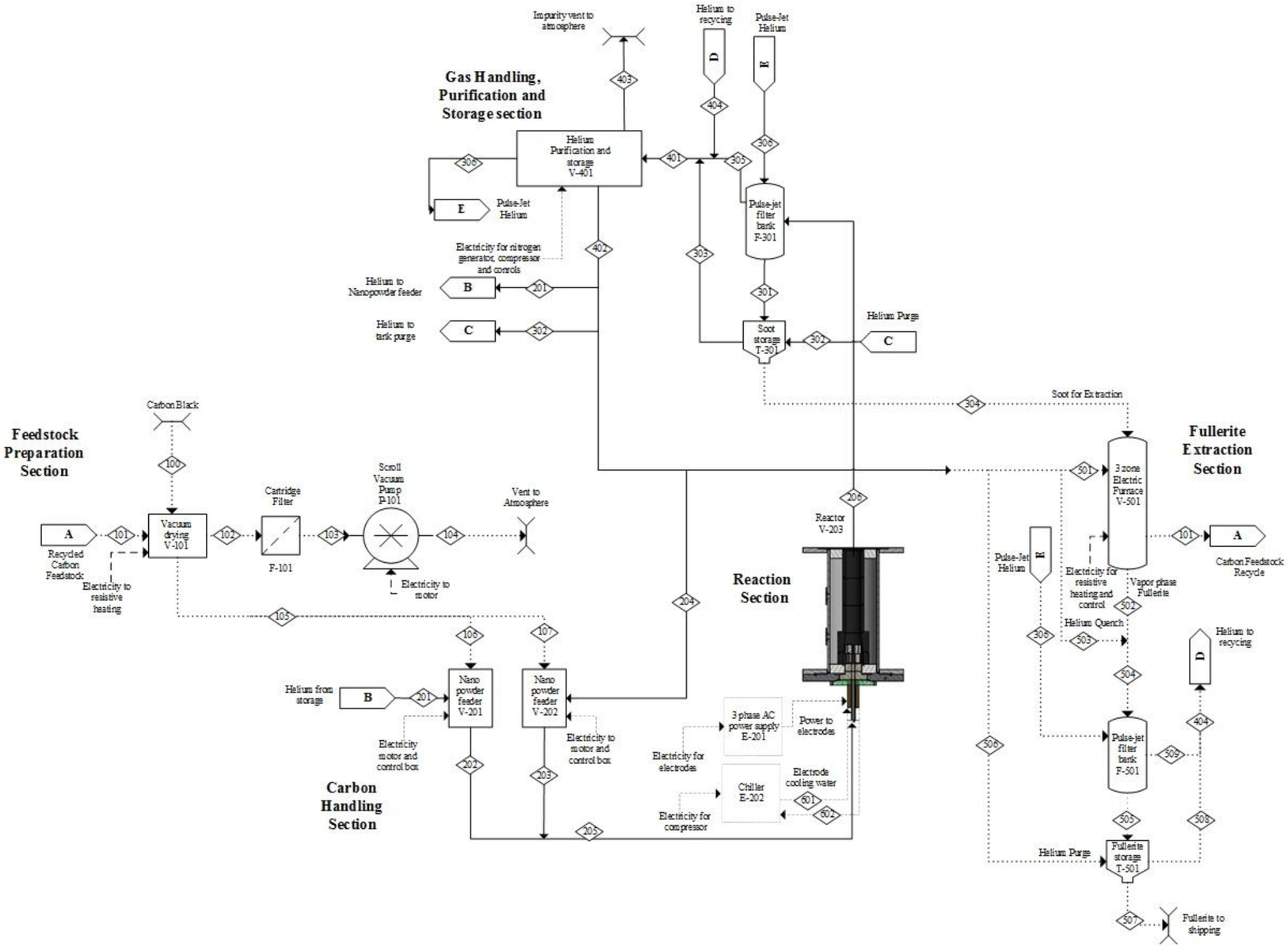


Legend	
1XX	Gas Handling
2XX	Carbon Handling
3XX	Reactor Section
4XX	Separation Section
5XX	Cooling Utilities

Instrument List			
Displayed Text	**Description**	**Connection Size**	**Manufacturer**
I-1	MKS Flowmeter	1/4"	MKS
I-2	MKS Flowmeter	1/4"	MKS
I-3	MKS Flowmeter for Quench gas	1/4"	MKS
I-4	MKS Flowmeter to Windows	1/4"	MKS
I-5	MKS Flowmeter to Powder feeder	1/4"	MKS

Equipment List				
Displayed Text	**Description**	**Manufacturer**	**Material**	**Model**
E-1	Tekna Nanopowder Feeder	Tekna	S.S	
E-2	MARK IV Plasma Reactor	Applied Nanotechnology Lab	Steel	Mark IV
E-3	Gas Filter	Applied Nanotechnology Lab	Steel	Mark IV

	Gas Handling System									Carbon Handling		Reaction Section				Separation Section				Cooling Utilities	
	101	**102**	**103**	**104**	**105**	**106**	**107**	**108**	**109**	**201**	**202**	**301**	**302**	**303**	**304**	**401**	**402**	**403**	**404**	**501**	**502**
Size	1/2"	1/2"	1/2"	1/2"	1/2"	1/4"	1/4"	1/2"	3/8"	1/2"	3/8"	1?4	1/4"	1/4"	2"	1/2"	2"	1/2"	-	3/8"	3/8"
Schedule	40	40	40	40	40	40	40	40	40	40	40		40	40	5	40	5	40	-	-	-
Phase (gas,liquid,solid)	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Solid	Solid	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Solid	Liquid	Liquid
Temperature (K)	300	300	300	300	300	300	300	300	300	300	300	300	300	320	373	373	300	300	300	288	298
Pressure (Psig abs.)	580	580	580	580	580	580	580	580	580	14	580	580	580	580	14	14	14	14	14	-	-
Gas Volumetric Flow (L/min)	17	-	17	-	17	4	1	12	12	-	-	4	1	12	13	-	17	17	-	-	-
Total Mass Flow rate (g/min)	2.8	2.8	2.8	-	2.8	0.7	0.1	2	2	-	0.48	0.7	0.1	2.28	2.38	-	3.08	2.8	0.28	3.8	3.8
Carbon Black (g/min)	-	-	-	-	-	-	-	-	-	-	0.28	-	-	0.28	0.26	-	0.26	-	0.26	-	-
Fullerite (g/min)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.02	-	0.02	-	0.02	-	-
Helium (g/min)	2.8	2.8	2.8	-	2.8	0.7	0.1	2	2	-	2	0.7	0.1	2	2.1	-	2.8	2.8	-	-	-
Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.8	3.8
			580																		



Stream Summary Table	Batch Carbon Handling								Continuous Carbon Handling & Reaction						Soot Separation Section						Gas Handling				Batch Soot Extraction								Cooling Water	
	100	101	102	103	104	105	106	107	201	202	203	204	205	206	301	302	303	304	305	306	401	402	403	404	501	502	503	504	505	506	507	508	509	601	602
Phase (gas, solid, liquid)	s	s	g	g	g	s	s	s	g	g	g	g	g	g	s	g	g	g	g	g	g	g	g	g	g	g	g	g	s	g	g	s	g	l	l
Temperature (K)	300	300	300	300	300	300	300	300	300	300	300	300	300	423	423	300	300	300	373	300	355	300	300	333	300	1100	300	333	333	300	300	300	333	283	303
Pressure (kpa)	100	100	10	10	10	100	100	100	100	100	100	100	100	100	100	100	100	100	100	400	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Volumetric flow rate (Lpm/min@ 25°C)	0.05	0.01	-	-	-	0.05	0.03	0.03	90	90	90	90	180	180	0	-	-	-	180	-	240	240	-	60	5	5	55	60	-	-	-	-	60	23	23
Mass flowrate(g/min)	119	31	-	-	-	150	75	75	14.7	17.8	17.8	14.7	35.6	35.6	6.2	-	-	6.2	29.4	-	39.24	39.24	-	9.84	0.82	1.82	9.02	12.1	2.3	-	2.3	-	9.84	23000	23000
Carbon Black	119	31	-	-	-	150	75	75	-	3.1	3.1	-	6.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
soot	-	-	-	-	-	-	-	-	-	-	-	-	-	6.2	6.2	-	-	6.2	-	-	-	-	-	-	-	-	-	2.3	2.3	-	2.3	-	-	-	-
Fullerite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.3	-	-	-	-	-	-	-	-	-
H20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Helium	-	-	-	-	-	-	-	-	14.7	14.7	14.7	14.7	29.4	29.4	-	-	-	-	29.4	-	39.24	39.24	-	9.84	0.82	0.82	9.02	9.84	-	-	-	-	9.84	23000	23000

Equipment List	
Process Vessels	
V-101	Vacuum Drying Oven
V-201	Nanopowder Feeder PFR400
V-202	Nanopowder Feeder PFR400
V-203	Mark IV Scaled up
V-401	Helium Purifier and storage
V-501	3 zone electric furnace for sublimation
Filters and Seperators	
F-101	Cartridge filter
F-301	Pulse-jet candle filter for soot seperation
F-501	Pulse-jet candle filter for fullerite seperation
Pumps	
P-101	Scroll vacuum pump
Electrical Equipment & cooling utilities	
E-201	3 phase AC plasma power supply
E-202	Water chiller
Storage tanks	
T-301	Soot storage tank
T-501	Fullerite storage tank

Legend:	
1XX	Batch Feedstock Handling
2XX	Carbon Handling and Reaction
3XX	Soot Seperation
4XX	Gas handling
5XX	Fullerite Extraction

Exiting Battery Limits

Entering Battery Limits

Batch Process Stream

Continuous Process Stream

Process Flow Diagram Prepared by:
Anshuman Sarawagi (ASARAWAG),
Applied Nanotechnology Laboratory.

Mark IV 10x scale up for preliminary economic analysis

University of New Brunswick
Department of Chemical Engineering

UNB

#	Revision	By	Date
0	Preliminary design	ASARAWAG	19-04-15

Curriculum Vitae

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Universities attended: BE Chemical Engineering, Manipal Institute of Technology, Manipal, India. 2009-2013

Publications: Hamady, M., Sheppard, D., Seddighi, K., Sarawagi, A., Scott, B., Wilcox, K., Chibante, L. (2015). Synthesis of nanocarbons using a large volume ac plasma reactor. Mrs proceedings, 1747.

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Novel process for Nanomaterial production using High-temperature Plasma's, 25th Graduate research conference, University of New Brunswick 2018.