Masters of the Flame

Nanostructured Carbon Products

2nd edition

Masters of the Flame: Chapter 1

Industrial Production of Fullerenes Becomes a Reality

"After 12 years of exciting research on fullerenes forming in flames at MIT," Jack Howard recalls, "my greatest thrill was seeing almost pure fullerenes coming directly from the combustion chamber at Nano-C." Dr. Howard is hardly given to hyperbole. On the contrary, the founder of Nano-C chooses his words as carefully as he controls the flame in a combustion reactor. It was in Howard's research labs at MIT that fullerenes were first made in combustion flames in 1991. That discovery, as one chronicler of fullerene research put it, marked "the day fullerene science came in from the cold." Twelve years later, another breakthrough discovery in the production of fullerenes by Howard and his team, this time at Nano-C, marked the day that an industrial production process for fullerenes—a scalable, low-cost method for producing fullerenes finally became a reality. This same Nano-C team, with a similar combustion technology, launched the manufacture of carbon nanotubes in 2003 creating an exciting new chapter in the "Masters of the Flame" story.

The potential uses for fullerenes have been accumulating at a remarkable rate since their discovery in the 1980s. Among these applications are solar cells, fuel cells, advanced skin care products, catalysts, and highly advanced polymer compounds. Yet, the cost of producing pure fullerenes has always been a barrier to commercialization. The first-generation technology for combustion synthesis, which was developed at MIT, held the promise of scaling up to industrial capacity, but the second-generation technology ("II-G") invented at Nano-C truly fulfills that promise. Oddly enough the cost of actually making the fullerenes is only a small portion of the total cost. The large majority of the cost is in the solvent-based post-processing. That post-processing purification is required because both the carbon arc method and the first generation combustion synthesis generate a mixture of 10% fullerenes and 90% of soot. By contrast, the II-G technology developed at Nano-C is able to produce purities of fullerenes above 90%, thereby eliminating the cost of purification for many applications and greatly reducing it for others. What's more, the II-G process is inherently scalable and highly efficient in ways the first generation is not. All this adds up to a true breakthrough to the low-cost production of fullerenes, a breakthrough the commercial world has been waiting for.

A New Form of Carbon

Fullerenes were discovered in 1985 and weren't available for study and characterization until 1991. Once they could be produced easily in very small quantities in the lab, it seemed that the scientific world had found a new darling. Previously the only two known forms of pure carbon were diamond and graphite. Here was a new molecular form of carbon in a unique sphere. In 1991 the prestigious journal Science named it "Molecule of the Year." That same year the

US National Science Foundation proclaimed the finding "the biggest chemical discovery since benzene in 1825." Thousands of scientific papers were published. Applications flooded government patent offices. At the beginning of 1993, the US Patent Office received more correspondence about fullerenes than about all other subjects combined. And in 1996, the three scientists who had discovered the fullerene molecule received the Nobel Prize in Chemistry for their contribution to the betterment of mankind.

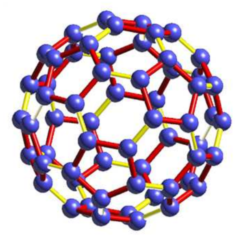
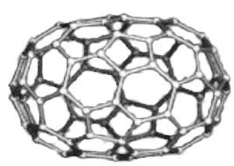
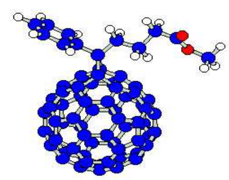
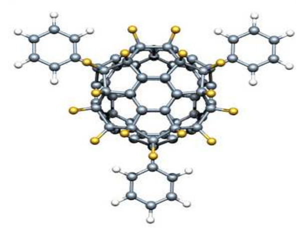
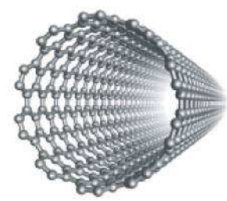
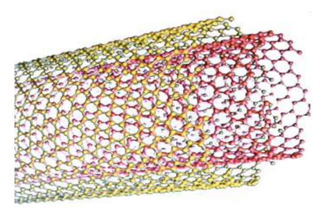
A World of Rich Chemistry

What so excited the imaginations of scientists both in the labs of academia as well as those of industry was the discovery of a naturally occurring, perfectly symmetrical ball of sixty carbon atoms. A C_{60} fullerene molecule is actually the shape of a soccer ball. It also resembles the complex configuration of Buckminster Fuller's geodesic domes. Given its shape, and given that chemists are known for the amusing names they give new creations, it is not that surprising that C_{60} came to be formally called "buckminsterfullerene," or, as scientists quickly nicknamed it, "the buckyball." The molecular group known as fullerenes actually contains other three-dimensional carbon molecules, including C_{70}, C_{76}, C_{78}, C_{84}, and higher fullerenes which could prove equally (or even more) interesting chemically than C_{60}. To date, however, all the major research and development efforts have been focused on C_{60}.

While the complex symmetry of fullerenes commanded the attention of the general public and press, for the chemist or the physicist, it was the unique properties of the closed cage of the molecule that opened a world of wonder and potential uses. The closed cage configuration is relatively taut and its natural tendency is to relax, which it can do by bonding with other atoms. Thus the closed cage of the fullerene provides a driving force for chemical reactions. This tendency, together with the particular way fullerenes are bonded, makes it very easy to add a large variety of chemical groups to fullerene cages. The fullerene + the chemical group is known as a "fullerene derivative." The structure of the cage and the bonding configuration also give fullerenes a high affinity for electrons, and, given the high number of bonding sites, make fullerenes uniquely potent as antioxidants.

These properties make them react very quickly and soak up a lot of free radicals. This unique ability allowed them to be called "radical sponges." In addition, the closed cage structure, with a molecular diameter of 0.7 nanometers, even permits other atoms to be placed inside. It is these properties of the fullerene's closed cage that have opened a world of rich chemical uses.

The National Science Foundation's comparison of the discovery of fullerenes with that of benzene is in fact very appropriate. Benzene, which forms a ring of carbon and hydrogen atoms (C_6H_6), became the basis for a whole branch of chemistry known as aromatic chemistry that has had an enormous impact on modern life. It is estimated, for example, that 90% of all pharmaceuticals produced today contain benzene rings. Because of the rich chemistry of this new form of carbon, it is expected that fullerenes will have an equally profound impact in a wide variety of applications. The new branch of chemistry based on fullerenes is already developed to the point where thousands of chemical derivatives have been made and whole textbooks are devoted to different aspects of the molecule. One indication of the significance corporate business sees in fullerenes is evidenced by Sony International. In

Fullerenes in a Nutshell		
People often confuse fullerenes with fullerene derivatives and both of those terms with carbon nanotubes.		
 **C_{60}**  **C_{70}**	 **PCBM**  **$C_{60}F_{15}(C_6H_5)_3$**	 **Single-walled Nanotube**  **Multi-walled Nanotube**
Fullerenes—A group of carbon molecules each having 60 or more carbon atoms in a closed cage configuration. C_{60}, the “buckminsterfullerene” or “buckyball,” has received the vast majority of research and development attention to date. However higher fullerenes, including C_{70}, C_{76}, C_{78}, and C_{84}, are also quite interesting and hold various promises in their own rights. Fullerenes are the third known form of pure molecular carbon after diamond and graphite.	**Fullerenes Derivatives—Molecules formed by a chemical reaction between fullerenes and other chemical groups. Fullerenes derivatives are also known as functionalized fullerenes. The market for derivatives is expected to mushroom because derivatives are the way to tailor fullerene molecules for particular products.**	**Nanotubes—Longer carbon molecules, which are a few nanometers thick and can be several microns long. Nanotubes can be a single-walled cylinder or can be multi-walled and contain concentric cylinders. Long strands of nanotubes can be woven to make very strong materials. The carbon-carbon bonds that characterize these molecules are thought by some scientists to be the strongest bonds known to man.**

2003 Sony announced that its R&D is moving away from the "twentieth-century era centered on silicon and to an era centered on carbon." It considers "fullerenes and various organic materials" as the symbols of this new age. In 2005, it announced a breakthrough in with fullerenes used in fuel cell membranes.

Creating Fullerenes by Combustion

Throughout the nineties, researchers relied on a simple laboratory process, the carbon arc method, for producing fullerenes. Chemists could easily use this method in their labs by setting up two carbon rods and running an electrical voltage between them, effectively vaporizing the carbon to form fullerenes and soot. The carbon arc method generated the small quantities sufficient for research; some development quantities were also available from suppliers who extended the carbon arc method. Nevertheless, the inefficiencies of the carbon arc method and the post-processing required to separate the fullerenes from the soot made the cost prohibitively high for commercial applications. The price for producing C_{60} through the carbon arc method did decrease through the nineties and leveled out at $25/gram ($25,000/kg) in 2001, where it has remained.

First Generation MIT Technology

Jack Howard knew that when fullerenes were needed in significant volume for commercial application, a combustion-based process held the key. For twelve years in his combustion research group at MIT, including significant contributions from a large number of graduate and undergraduate students, Dr. Howard led research on the production of fullerenes by combustion. In 2001, with the encouragement of MIT's Technology Licensing Office, he founded Nano-C and licensed the MIT combustion method for producing fullerenes.

In the meantime, Mitsubishi Chemical in conjunction with Mitsubishi Corporation, became interested in the commercial potential for fullerenes. Mitsubishi Corporation had actually built a pilot plant based on the carbon arc method. In 2001, after Dr. Howard founded Nano-C, Mitsubishi Chemical approached Nano-C about the commercial viability of the MIT technology and the possibility of licensing it. In November of 2001, Mitsubishi Corporation formally requested and Nano-C granted a non-exclusive license to manufacture fullerenes using the first generation technology in Japan and to sell the product outside of the US and Europe. Frontier Carbon, a Mitsubishi affiliate, is now operating a facility based on the first generation combustion synthesis process. Mitsubishi says that the facility, which was expanded in June 2003, has a capacity of 40 metric tons/year.

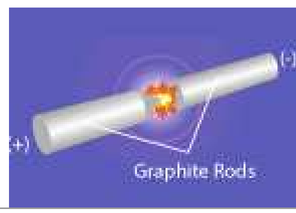
The 1991 MIT first generation technology can only achieve industrial scale by incrementally building larger versions of the same type of burner and then replicating it, that is, building more burners. This way of scaling up does not afford the usual economies of scale. Nevertheless Mitsubishi has validated the basics of the combustion synthesis method as an industrial process and their leadership in the Japanese market has helped generate broad interest in the large-scale use of fullerenes. This first-generation technology is sufficient near-term for the needs of some high-end applications. However, it can provide neither the bulk quantities nor the cost reductions required for truly high volume applications.

Second Generation (II-G) Nano-C Technology

Nano-C's II-G technology for the combustion–based production of fullerenes is a breakthrough because it provides high purity and high throughput simultaneously, thereby reducing the cost of fullerenes to one-tenth (or less) the cost of the first generation process. Dr. Howard and his team accomplished this remarkable achievement through two years of intense effort using the advanced knowledge developed through years of research at MIT on the nature of fullerene formation and the optimal conditions for their production in combustion. Nano-C's team can operate the combustion process in such a way that it produces purity levels of 95+%. Moreover they can control the process precisely enough to generate various mixes of C_{60}, C_{70}, and the higher fullerenes or to produce just C_{60} or C_{70} by the ton. This degree of control means that they can tailor the product to a particular customer's demand without the need for expensive solvent-based post-processing. Companies need only buy the exact type or mixture of types that their manufacturing process requires.

Another factor in the dramatic reduction of the cost to produce fullerenes stems from the high throughput, that is, the velocities at which fuel is fed into the reactor. Making fullerenes requires low (sub-atmospheric) pressure, and, in conventional reactors, pressure directly affects throughput. (If the pressure, for example, is one-twentieth of atmospheric pressure, then ordinarily the throughput would be one-twentieth of that possible at atmospheric pressure.) What Nano-C has achieved through its sophisticated new combustor design is high throughput at low pressure, something which had never been done before. Based on the pilot reactor in development at Nano-C, the team foresees enormous gains—**more than ten times the throughput** of the first generation technology.

Scalability was another goal Nano-C knew it had to realize. Jack Howard explains the inherent scalability of the II-G process this way: "We knew how to go about establishing a scalable process. Our new combustor design is much larger than the first generation MIT reactor but more importantly it has the features that enable you to easily scale up to industrial production. You could not do that with the first generation, MIT technology and reactor." Behind the II-G process are years of research and understanding of the complex and delicate rules for combustion synthesis of fullerenes accumulated at MIT and developed at Nano-C. That research and understanding benefited from previous work on combustion chemistry, as well as from the use of computers for advanced mathematical modeling of over 1000 discrete chemical reactions.

The Evolution of Fullerene Manufacturing Technology			
	Carbon Arc	1st Generation Combustion	2nd Generation Combustion
Inventors	Kratchmer-Huffman/UA THE UNIVERSITY OF ARIZONA.	Howard/MIT MIT	nano-c
Synthesis	Individual graphite rods are vaporized with electrical currents in low pressure inert gas. 	A continuous low flow of hydrocarbon fuel is burned at low pressure in a "flat" flame. 	A continuous high-flow of hydrocarbon is burned at low pressure in a 3 dimensional chamber. 
Fullerene Extraction	Solvents are used to separate fullerenes from other combustion byproducts.	Solvents are used to separate fullerenes from other combustion byproducts.	Generally not necessary
Projected Price of Mixtures	>$10,000/kg	<$1,000/kg	<$200/kg
Fullerene Separations	High Pressure Liquid Chromatography (HPLC) using solvents.	High Pressure Liquid Chromatography (HPLC) using solvents.	Not Necessary
Projected Price of C_{60}	>$25,000/kg	<$16,000/kg	< $200/kg
Capital to Scale	$$$	$$	$

Fullerene Commercialization

Nano-C believes that it is important to leave the hype and hope of the early nineties well behind, particularly now that the nascent fullerene industry is moving into the commercial phase. The price for fullerenes is coming down and will decrease further when Nano-C completes a scale-up to a multi-ton facility. As the price decreases, more commercial applications will create greater demand in the marketplace. There are already some products in late-development or early commercial stages. These commercial efforts take advantage of the electronic, antioxidant and reactive properties of fullerenes that make them especially suitable for use in polymer photo-voltaic applications, polymer electronics, skin care products, catalysis and in polymeric compounds.

Chapter II: Masters of the Flame Make Carbon Nanotubes

Filamentary carbon structures, or fibers, that may have included carbon nanotubes (CNTs) were observed as early as the 1950s. In 1991 Sumio Iijima, a researcher at the NEC Laboratory in Japan observed that these fibers were hollow. The diameter of a nanotube is on the order of one nanometer, many times smaller than the width of a human hair, but up to several microns long. CNTs come in two principal forms, single-walled (SWCNT) and multi-walled (MWCNT). Conceptually, the structure of a SWCNT is a one-atom-thick layer of graphite called graphene that is wrapped into a seamless cylinder with either open or closed ends. As their name implies, MWCNTs consist of multiple concentric layers of graphene that form a tube shape, as pictured earlier.

Soon after Iijima's discovery, the Howard research group at MIT extended the combustion method for fullerenes production to include the combustion synthesis of SWCNTs. This new method of nanotube production is now being commercialized by Nano-C is yet another step-change in the technology of carbon nanomaterials.

The advantage of Nano-C's carbon nanotube technology is intrinsic due to its exothermic nature and internal generation of the growth species from an easily handled hydrocarbon fuel such as natural gas. It does not use high pressure CO and as it is exothermic, it does not require external energy. These attributes combined with its multiple degrees of freedom in operating conditions, i.e., fuel type, pressure, temperature, type & particle size of catalyst, fuel-oxygen ratio, dilution with inert gas, and cold gas velocity make Nano-C's process unique in its range of cost, flexibility, scalability and reproducibility when compared to the competing alternatives. With this inherent advantage, Jack Howard and his colleagues at Nano-C believe that combustion-based manufacturing will become the dominant technology when considering producing quantities beyond research and development requirements and when economies of scale matter. Clearly, the field of nanostructured carbon products will never be the same.

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When asked about completing Chapter I and II, Dr. Howard replied, "it is an exciting story that continues to unfold."

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