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Fullerenes on Ion Engine Propellant Applications

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EFFECT OF THE THERMAL STABILITY AND REACTIVITY OF FULLERENES ON ION ENGINE PROPELLANT APPLICATIONS

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Abstract

Because vapor phase fullerene molecules collide with high temperature surfaces at both the cathode in DC discharges and at the walls of vapor sources, knowledge of the thermal stability and material compatibility of fullerenes is important for ion thruster applications. Here, we present a study of the high temperature behavior of fullerenes. We find that when C₆₀ and C₇₀ are maintained at temperatures above 1073 K, or are exposed to hot metal surfaces, significant degradation occurs. We find an activation energy of 261.5 kJ/mol for this process. At temperatures below 873 K, no breakdown of fullerenes can be detected, even after heating for 6 hours. The effect of these findings on C₆₀ ion thruster design is discussed. Our present C₆₀ RF ion thruster experiment is also described.

Background

Since 1991, three groups¹⁻³ have reported on the development of an ion thruster which utilizes the all-carbon molecules known as fullerenes as a propellant. Discussions of the potential performance advantages of fullerene fueled ion propulsion have been published^{4,5}. Anderson and Fitzgerald,³ and Hrubby et al.¹ both successfully sustained DC fullerene plasma discharges using thoriated tungsten filament cathode ion sources. Anderson and Fitzgerald confirmed the presence of fullerene ions by mass spectral analysis of the extracted ion beam. Hrubby et al. detected fullerene material deposited on optical surfaces using Fourier Transform Infrared (FTIR) spectroscopy. Both of these groups reported substantial erosion of the filament cathodes used in their devices. The presence of a significant quantity of toluene insoluble carbonaceous material was observed in the effusion cell by both groups after heating.

Takegahara and Nakayama² have reported an unsuccessful attempt to establish an RF generated plasma using

fullerenes. They found that their quartz discharge chamber wall temperature was too low, resulting in condensation of the fullerene propellant. Takegahara and Nakayama obtained FTIR absorption spectra of original and condensed C₆₀ powder. If normalized, their spectra indicate a loss of material similar to that observed by Hrubby et al. and Anderson and Fitzgerald.

Hrubby et al.¹ carried out tests of fullerene material compatibility with stainless steel, molybdenum, alumina, boron nitride, aluminum nitride, and quartz. They reported that no reaction of the fullerenes occurred with any of these materials, but chose quartz for their discharge chamber with molybdenum and stainless steel grids. Anderson and Fitzgerald³ used both graphite and stainless steel sources and grids. In both sources, notable degradation of the propellant molecules at high temperature was confirmed by FTIR spectroscopic analysis of the powder remaining in the effusive cell and on the walls of the discharge chamber. However, mass spectral analysis of the ion beam did not indicate the presence of either C₂ or C₄ fragments which would be expected from dissociated fullerenes.⁶ It was also found that removal of residual solvents and impurities by heating the mixed fullerene samples under dynamic vacuum at 473 K for 12 hours prior to operation of the discharge did not inhibit the fullerene breakdown.

Though not exploring any particular application, H. Yu et al.⁶ investigated the formation and fragmentation of fullerene ions in an electron-irradiated ion source. Unimolecular dissociation rate constants for the process of fragmentation via removal of *c.v.c.n*-numbered carbon fragments were obtained.

Because propellant flow rate is determined by the fullerene vapor source temperature, knowledge of the reactivity and stability of C₆₀ and C₇₀ molecules at high temperatures is important to fullerene ion thruster development. Excessive degradation will impact the total propellant utilization efficiency, as well as increase the possibility of thruster failure due to the presence of condensed fragments and

reaction products. The fullerene sources may require heating to over 800 K for adequate fullerene pressures to be obtained. Figure 1 shows experimentally-determined vapor pressure curves for C₆₀ and C₆₀/C₇₀ mix. Following cathode operation with fullerene vapor for either DC plasma generation or ion beam neutralization would require that C₆₀ be stable at temperatures over 1300K. It is apparent that an in-depth look at the high temperature behavior of fullerenes is required.

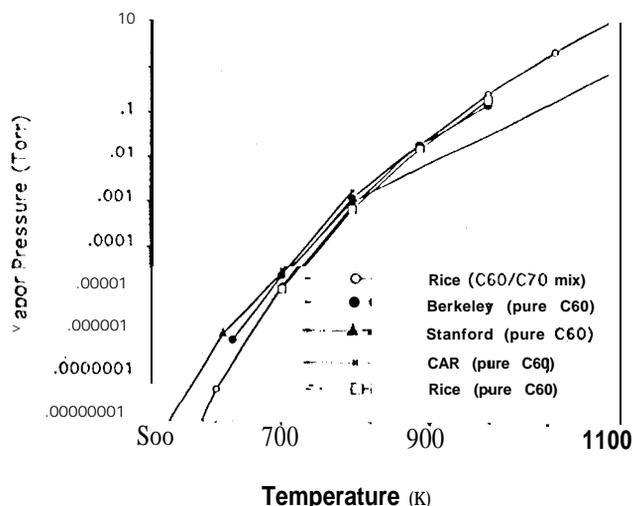


Figure 1. Vapor pressure as a function of temperature for C₆₀ and C₆₀/C₇₀ mix.⁷⁻¹⁰

Thermal stability and material compatibility of C₆₀ and C₇₀

There have been numerous studies of the oxidative behavior of C₆₀ and C₇₀¹¹ conducted since fullerenes became available in macroscopic quantities in 1991. Experimental¹⁷ and theoretical¹⁸ investigations of thermal decomposition of fullerenes have also been reported.

Sundar et al.¹⁷ sealed pellets of C₆₀ in evacuated ampoules and heated them to temperatures between 773 K and 1173 K for 24 hours. X-ray diffraction and UV-visible absorption spectra of the samples showed increasing degradation with higher temperature. However, adequate preheating of the samples under dynamic vacuum to remove solvents and adsorbed impurities was not performed, nor has such a study been conducted where the decomposition in vacuum was evaluated as a function of time.

The reactivity of C₆₀ with metals is of interest to the high temperature superconductor community. Alkali-metal-doped fullerenes have the highest known superconducting transition temperatures for organic superconductors. Thus, the interaction of C₆₀ with alkali metals at temperatures below 500 K has been investigated^{9,20} in attempts to form compounds.

There are several possible mechanisms for C₆₀ degradation. These are 1) thermal disintegration (vibrational modes excited beyond bond-strength limitations), 2) stoichiometric reaction with impurities, 3) catalysis with impurities, 4) catalysis with container walls, 5) catalysis with amorphous carbon fragments, or 6) a combination of any of the preceding mechanisms.

Zhang et al.¹⁸ have reported molecular dynamics simulations modeling the process of thermal disintegration of fullerenes. They predict fragmentation temperature as a function of cluster size for fullerenes containing 20 to 90 atoms. Not surprisingly, C₆₀ and C₇₀ were shown to be more thermally stable than other fullerenes. It was also found that the disintegration temperature became reasonably constant for molecules containing more than 60 carbon atoms. Zhang et al. interpreted the fragmentation temperature as a measure of the weakest bond in the molecule. Hence, their fragmentation temperature corresponds to the onset of bond-breaking in the fullerene cage.

The predictions of Zhang et al.¹⁸ agree quite well with measurements of the enthalpy of formation of C₆₀ reported by References 21-23 to be 2.30 X 10³ kJ/mol, 2.28 X 10³ kJ/mol, and 2.42 X 10³ kJ/mol, respectively. Using the interpretation of Zhang et al. of thermal disintegration, we find a lower limit of an Arrhenius activation energy for the process to be 38.3 kJ/mol, corresponding to a temperature of 4610 K.

A.M. Vassallo et al.² performed an emission FTIR study of solid-state C₆₀ and determined thermal stability of the material at the highest temperature of their experiment, 873 K. Significant sublimation of the fullerene material appears to have made the experiment impractical at higher temperatures. When a 25% oxygen in argon mixture was introduced to the C₆₀ sample during heating, all C₆₀ emission peaks were seen to disappear by 723 K. CO₂ and CO emission bands were observed, as well as features from reaction products that may be attributed to cyclic anhydrides.

Experiment

We have performed detailed fullerene thermal and material compatibility tests to determine the source of residue in fullerene ion thruster experiments. The tests were performed by placing approximately 10 mg of fullerene powder in quartz ampoules cleaned in acetone and freon. We prepared sets of 5 ampoules at a time containing either pure C₆₀ obtained from MFR Corporation, pure C₇₀ from Term LTD., or a fullerene mix composed of approximately 85% C₆₀ and 15% C₇₀. The fullerene mix was Soxhlet extracted with toluene from soot produced by Ulvick industries.

The ampoules were placed under vacuum in the low 10⁻⁶ Torr range. Partial pressures of monatomic and diatomic oxygen, CO, CO₂, O₁₁, H₂O, toluene, and benzene were monitored using a calibrated MKS model 600A PPT Residual Gas Analyzer (RGA). Mass spectra of all contaminants (under 100 amu) in the vacuum system were also obtained.

The fullerene samples were heated to 473 K for 3 hours, then to 523 K for an additional 1 to 3 hours, until the partial pressure of toluene fell below 2x10⁻⁸ Torr. Figure 2(a,b,c) shows 10 minute RGA scans initiated upon heating of the ampoules containing C₇₀, C₆₀, and fullerene mix samples, respectively. In all cases, there was a rapid and significant increase in toluene partial pressure, with moderate increases in O₂ and H₂O. C₆₀ epoxide may have been another source of the observed oxygen. In the case of the C₇₀ samples, both CO₂ and CO partial pressures increased more rapidly than they did during either the pure C₆₀ or mixed fullerene sample heating. The total pressure in the vacuum system subsequently increased beyond 2x10⁻⁴ Torr (the upper limit of the range of the RGA) for several minutes after the ampoule heaters had reached steady-state temperatures.

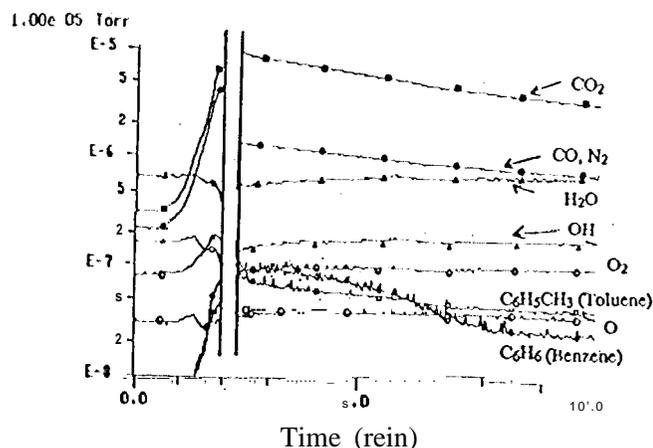


Figure 2a. 10 minute RGA trace of partial pressures for C₇₀ anneal.

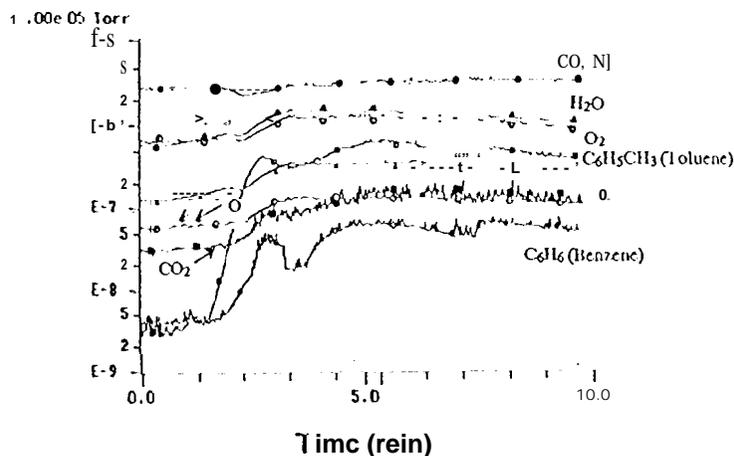


Figure 2b. 10 minute RGA trace of partial pressures for C₆₀ anneal.

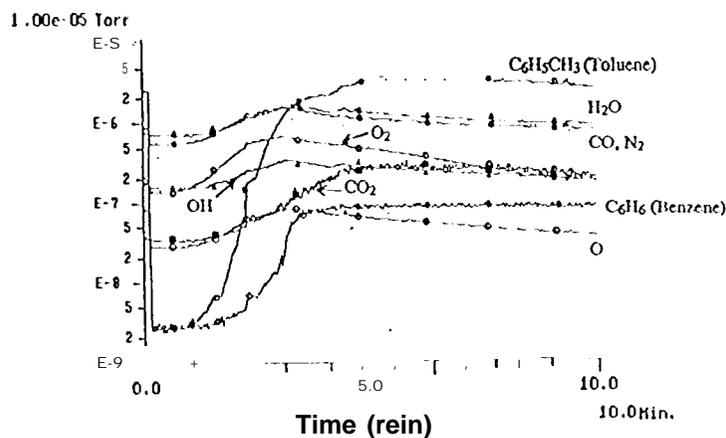


Figure 2c. 10 minute RGA trace of partial pressures for C₆₀/C₇₀ mix anneal.

The anneal temperature we used for solvent removal from the fullerenes in the quartz ampoules was between 473 K and 523 K. Although this temperature is high enough to remove a significant portion of adsorbed water on the surface of the ampoule, it is insufficient for removal of the hydroxyl groups terminating the quartz surface. It is necessary to heat the quartz under dynamic vacuum to over 873 K to remove these surface impurities in the form of H₂O and H₂.²⁴ To determine whether these sites on the quartz surface were serving as catalysts for the fullerene decomposition, we formed an ampoule with a "pocket" for holding the fullerene test sample while the bottom portion of the ampoule was heated with an acetylene torch. The remainder of the experiment was performed as before.

The ampoules were then vacuum sealed and placed in a tube furnace for durations of 20 minutes, 1 hour, 3 hours and 6

hours, We prepared sets of samples heated to 873 K, 973 K, 1073 K, 1173 K, 1273 K, and 1473 K. One trial consisted of ampoules that had been backfilled with approximately 5 Torr of Helium.

For total elimination of toluene impurities, Milliken et al.¹¹ found that heating of C₆₀ to 483 K for 16 hours was sufficient. To verify that the four to six hour bake was adequate to drive off contaminants, we heated five samples of the fullerene mix under dynamic vacuum for 16 hours at 473 K and compared these samples with those heated for shorter durations.

To study the effect of bulk metals in contact with fullerenes at high temperatures, we placed 5.0 cm long by 0.32 cm wide metal strips in the ampoules with the fullerenes. Tungsten, molybdenum, tantalum, and 304 series stainless steel samples were etched in a nitric acid solution for 1 minute, rinsed and then dried under nitrogen before being placed in the ampoules. Only the stainless steel sample was visibly altered after heating to 1073 K. It was coated with a black residue which, when rinsed away, revealed a dulled surface. Table 1 is a list of the samples analyzed in this study.

UV-VIS Absorption Analysis

Analysis of the samples was performed by UV absorption spectroscopy using a Cary UV-VIS-NIR spectrophotometer (model 5F). A 1.0 cm path length was used in double beam mode with blank solvent in the reference beam path. The powder samples were placed in 200 ml of methylene chloride and sonicated. A further dilution of 1:10 was made for analysis. The concentration of C₆₀ was determined by monitoring the 270 nm absorption feature. The peak intensity was corrected for initial sample weight, then correlated to remaining fullerene material.

Significant quantities of seemingly insoluble material were observed in the CH₂Cl₂ solutions after sonicating for several hours. The volatility of C₆₀ in CH₂Cl₂ was reported by SR125 as 0.26 mg/ml. However, we found that some of the solid was in fact soluble in toluene. Due to UV absorption below 250 nm in toluene, only the 330 nm peak in the C₆₀ absorption spectrum could be used for analysis of toluene dissolved samples. We prepared two pure C₆₀ solutions - one in toluene, the other in methylene chloride - to compare the concentration in each solvent. The concentration of C₆₀ in the methylene chloride was found to be approximately 10% below that in the toluene even though identical preparation procedures were used. The concentration of mixed fullerene in the toluene control samples was found to be 77.6 ± 3.5 A cc/mg. The main

sources of error were: (c) stability of dilution preparation and mass uncertainty.

Results

Figure 3 shows the UV absorption spectrum of mixed fullerene samples heated at 1073 K for various durations. These samples were prepared in methylene chloride.

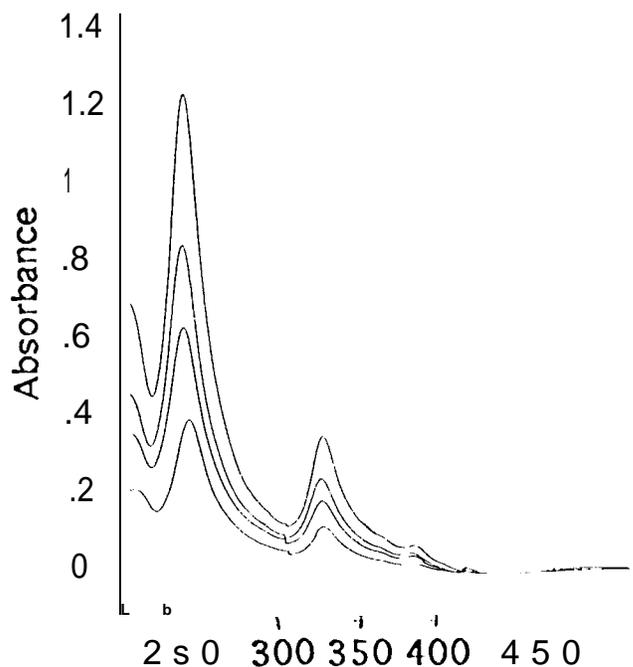


Figure 3. UV absorption spectra of fullerene mix heated for various durations at 1073 K.

Figure 4 shows the degradation rate of the samples mentioned above, toluene dissolved samples with a helium backfill, and samples preheated for 16 hours at 473 K. Note that there is no significant difference in the degradation rates. The samples that had been heated to temperatures greater than 1273 K completely decomposed. This toluene insoluble material was examined with x-ray diffraction. The only diffraction peaks to appear were very faint and were attributed to zinc impurities. Though no diffraction pattern from the carbonaceous material could be obtained, the material looked distinctly crystalline. A scanning-electron-microscope image of this material is shown below in Figure 6; it does not appear amorphous. We do not yet have an

explanation for the lack of diffraction peaks attributable to this material.

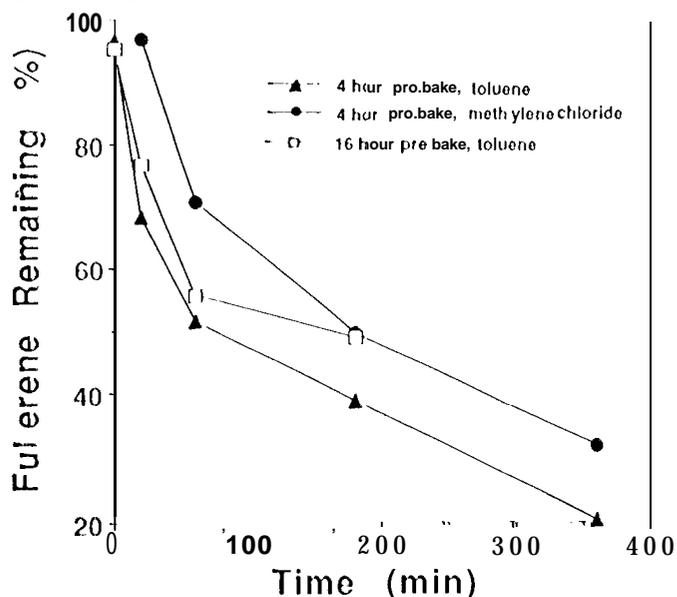


Figure 4. Percent age of fullerene mix remaining as a function of time. Samples heated to 1073 K,

Figure 5 is a plot of the percentage of toluene soluble material remaining as a function of temperature. Note the apparent stability of the fullerene up to about 973 K.

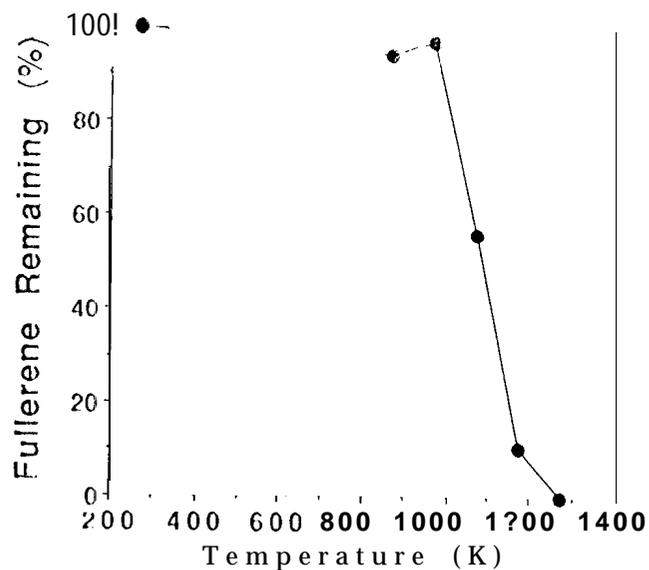


Figure 5. Percentage of fullerene mix remaining as a function of temperature. Samples heated for one hour.



Figure 6. SEM image of insoluble carbon residue from quartz ampoule heated to 1273 K for 1 hour.

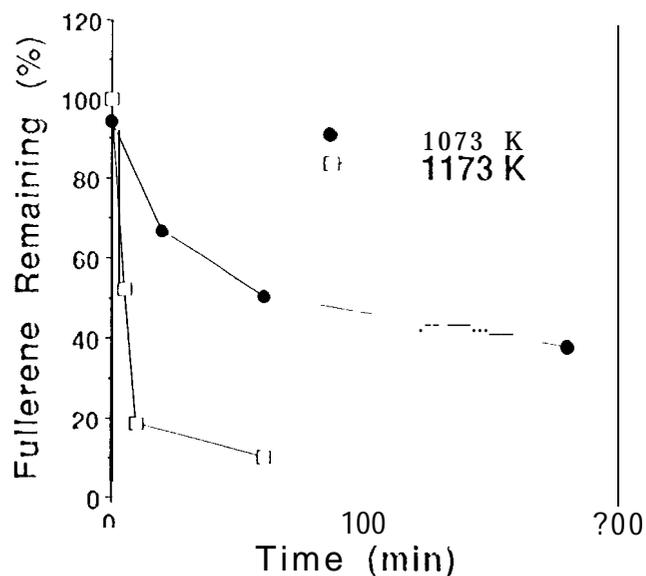


Figure 7. Decay curves for toluene-prepared samples at 1073 K and 1173 K.

	Initial Mass (mg)	Composition	Temperature (K)	Time (min)	Solvent	peak (nm)	A cc/mg
5/15/94							
1	9.5	C ₆₀ /C ₇₀	---	---		330/270	219
2	13.0	C ₆₀ /C ₇₀	1073	360	CH ₂ Cl ₂	330/270	21.5/70.7
3	10.0	C ₆₀ /C ₇₀	1073	180	CH ₂ Cl ₂	330/270	32.0/110.0
4	10.5	C ₆₀ /C ₇₀	1073	60	CH ₂ Cl ₂	330/270	45.7/156.0
5	13.4	C ₆₀ /C ₇₀	1073	20	CH ₂ Cl ₂	330/270	61.7/213.0
5/16							
1	11.1	C ₆₀ /C ₇₀	---	---	CH ₂ Cl ₂	270	128
2	11.6	C ₆₀ /C ₇₀	---	---	CH ₂ Cl ₂	270	143
3	11.0	C ₆₀ /C ₇₀	---	---	CH ₂ Cl ₂	270	127
4	10.4	C ₆₀ /C ₇₀	---	---	CH ₂ Cl ₂	270	111
5	10.8	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃	330	66.6
5/17 no.1							
1	11.2	C ₆₀ /C ₇₀ .He	---	---	C ₆ H ₅ CH ₃	330	75.0
2	9.2	C ₆₀ /C ₇₀ .He	1073	180	C ₆ H ₅ CH ₃	330	30.4
3	10.6	C ₆₀ /C ₇₀ .He	1073	60	C ₆ H ₅ CH ₃	330	40.0
4	8.3	C ₆₀ /C ₇₀ .He	1073	20	C ₆ H ₅ CH ₃	330	53.0
5	8.8	C ₆₀ /C ₇₀ .He	1073	360	C ₆ H ₅ CH ₃	330	15.9
5/19							
2	9.0	C ₆₀	---	---	CH ₂ Cl ₂	330	64.4
3	10.1	C ₆₀	---	---	C ₆ H ₅ CH ₃	330	71.3
5/20							
1	8.1	C ₇₀	---	---	CH ₂ Cl ₂	380	212.3
2	8.6	C ₇₀	---	---	CH ₂ Cl ₂	380	148.8
3	9.5	C ₇₀	---	---	CH ₂ Cl ₂	380	138.9
4a	10.4	C ₇₀	1073	180	CH ₂ Cl ₂	380	125
5	9.5	C ₇₀	1073	360	CH ₂ Cl ₂	380	105
5/24							
1	9.8	C ₆₀ /C ₇₀ .M	1073	60	CH ₂ Cl ₂	270	165
2	11.2	C ₆₀ /C ₇₀ .T*	1073	60	CH ₂ Cl ₂	---	---
3	10.5	C ₆₀ /C ₇₀ .W	1073	60	CH ₂ Cl ₂	270	78.1
4	11.3	C ₆₀ /C ₇₀ .SS	1073	60	CH ₂ Cl ₂	270	95.6
5	9.9	C ₆₀ /C ₇₀	1073	60	CH ₂ Cl ₂	270	107.1
5/25 no.1							
1	11.6	C ₆₀ /C ₇₀ .SS	1273	60	C ₆ H ₅ CH ₃		
2	12.0	C ₆₀ /C ₇₀ .SS	873	120	C ₆ H ₅ CH ₃	330	72.6
5/25 no.2							
1	9.6	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		
2	9.9	C ₆₀ /C ₇₀	1273	60	C ₆ H ₅ CH ₃		77.1
3	9.7	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		74.7
4	10.5	C ₆₀ /C ₇₀	873	60	C ₆ H ₅ CH ₃		76.3
5	9.5	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		see below
5/27							
1	14.6	C ₆₀ /C ₇₀	untreated	---	CH ₂ Cl ₂	270	156
5/25 #5							
1	9.5	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		80.6
2	9.5	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		83.0
3	9.5	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		80.6
4	9.5	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		75.7
5	9.5	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		75.7
6	9.5	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃		80.6
6/7 no.1							
1	9.9	C ₆₀ /C ₇₀	---	---	C ₆ H ₅ CH ₃	330	75.7
2	10.8	C ₆₀ /C ₇₀	1073	20	C ₆ H ₅ CH ₃	330	61.1
3	9.1	C ₆₀ /C ₇₀	1073	60	C ₆ H ₅ CH ₃	330	44.2
4	9.7	C ₆₀ /C ₇₀	1073	180	C ₆ H ₅ CH ₃	330	39.2
5	9.6	C ₆₀ /C ₇₀	1173	60	C ₆ H ₅ CH ₃	330	8.2
6/7 no.2							
4	9.2	C ₆₀ /C ₇₀	973	60	C ₆ H ₅ CH ₃		77.0
5	9.8	C ₆₀ /C ₇₀	873	360	C ₆ H ₅ CH ₃		80.1
6/7 no.3							
1	10.2	C ₆₀ /C ₇₀	1173	5	C ₆ H ₅ CH ₃	330	41.5
3	9.7	C ₆₀ /C ₇₀	1173	10	C ₆ H ₅ CH ₃	330	14.9

Table 1. Fullerene samples prepared for material compatibility and thermal stability tests

By fitting the fullerene decay curves shown in Figure 7, we obtained decay constants, $k(T)$, which were then used to find an Arrhenius activation energy for the disintegration as in the equation,

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

where A is the frequency factor (assumed constant here), E_a is the activation energy, R is the gas constant, and T is the temperature.

Rascal on the work reported in References 21-23, and assuming the definition of fragmentation used by Zhang et al.,¹⁸ we would expect the lower limit of the activation energy to be about 40.0 kJ/mol for thermal decomposition if a Lindemann mechanism²⁶ is responsible. In fact, the activation energy for this process is found to be 261.5 kJ/mol - a number higher than that predicted by Zhang et al.

Therefore, it is possible that we are observing thermal disintegration of the fullerene mix.

Diffuse Reflectance FTIR Spectroscopic Analysis

Diffuse reflectance FTIR spectroscopy was also used to analyze the decomposed material. Figure 8(a,b,c) shows three spectra: one of untreated fullerene mix, a sample heated to 1073 K for 1 hour, and a sample that had been heated for 18 hours at 523 K in nitrogen and air. Note the appearance of cyclic anhydride features in the 1800-1000 cm^{-1} region of Figure 7c similar to those observed by Vassallo et al.¹² However, no oxidation products are evident in the 1073 K sample, although only 50% of the material remained as fullerene. Hydrocarbon impurities are evident in all of the samples. Also, there is a possibility that at these temperatures any intermediate acids will have decomposed, leaving only CO_2 and CO as reaction products and catalysts. We have not attempted to determine whether these gases are present in the sealed ampoules after heating.

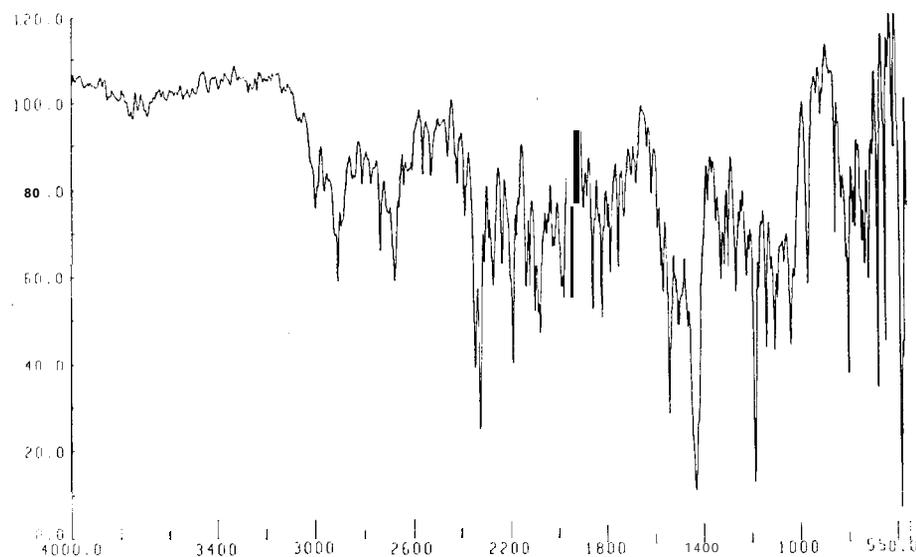


Figure 8a. FTIR spectrum of $\text{C}_{60}/\text{C}_{70}$ Untreated

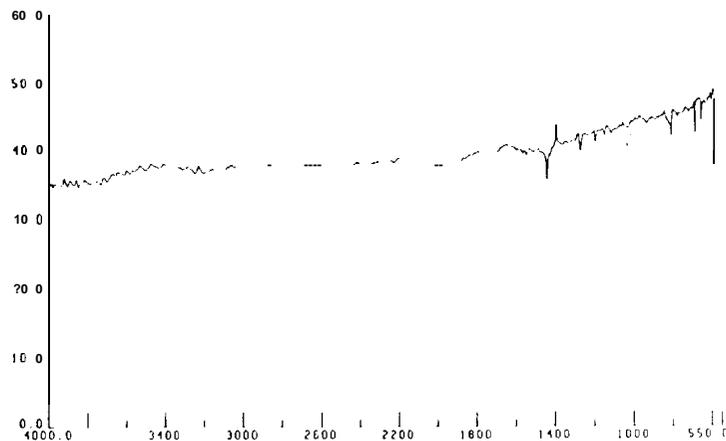


Figure 8b. FTIR Spectrum of C₆₀/C₇₀ heated for 1 hour at 1073 K

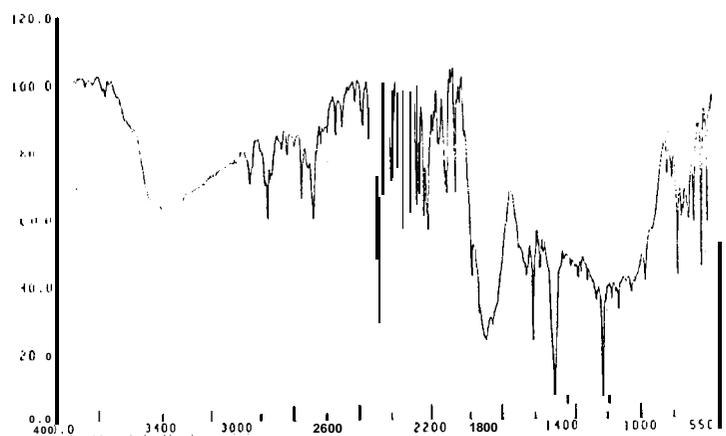


Figure 8c. FTIR Spectrum of C₆₀/C₇₀ heated in N₂ and air for 18 hours at 523 K

Analysis of fullerene samples using infrared spectroscopy is a very useful technique, but we have found it should be used with caution in accordance with the following observations. Carbon black soot is so strongly absorbing in the IR that very low baselines may be observed. This will obscure the fullerene peaks and make quantitative analysis difficult if too much soot is present. Also, some peaks in the IR spectrum might be misconstrued as adsorbed impurities, specifically CO₂. The latter has been reported in publications showing IR absorption spectra of C₆₀^{2,7*}. These spectra showed moderate intensity peaks in the region where CO₂ twin features are typically observed. These features which appear at 2349 cm⁻¹ and 232.8 cm⁻¹ were attributed to CO₂ adsorbed by the fullerene. However, the peaks are shifted and their relative intensities switched from commonly observed CO₂ combination features.

To investigate this discrepancy, we performed diffuse reflectance FTIR on fullerene samples prepared by three separate techniques: films formed on KBr by vacuum evaporation, freshly formed fullerene containing soot transported with ascorbic acid (a CO₂ absorber), and purified C₆₀ obtained from MTR Corporation dissolved in CS₂. It is

each of the samples should have been free of CO₂ contamination, the twin peaks were present in all three spectra with the same relative intensity. Therefore, we believed that the features were due to either combination modes or vibrational modes allowed by the presence of ¹³C isotope.

Several papers have since been published^{29,30} which show the very rich vibrational spectrum of C₆₀. Theoretically predicted modes are assigned to each observed peak, including those originally attributed to CO₂. However, these peak assignments have not yet been confirmed by analysis of isotopically enriched or isotopically pure fullerenes. We have attempted formation of pure ¹³C fullerenes by laser vaporization techniques, but found no toluene extractable material in the soot. Subsequently, we attempted to form isotopically enriched fullerenes by the arc method. Hollow graphite rods were packed with amorphous ¹³C powder mixed with a carbon binder. Though fullerenes were produced from these rods, no peak shifting or growth was observed in the spectrum. We believe that only the graphite portions of the rod actually vaporized and contributed to fullerene formation. We are continuing our attempts at producing isotopically pure fullerenes by compressing amorphous carbon powder at high

temperatures to form rods for arc method fullerene production. This technique has been successfully employed³¹ to demonstrate peak shift of the four main dipole peaks of C₆₀.

RF Plasma Discharge Experiment

To avoid the presence of high temperature metal surfaces other than the extraction grids, we have constructed an RF discharge chamber similar to that of Takegahara and Nakayama². We are using an Ioni Power Systems 13.56 MHz RF power generator (model 600A) and impedance matching circuit (RF Services) to reduce reflective RF losses from the engine. A schematic of the RF thruster assembly is depicted in Figure 9.

The discharge chamber consists of a 7.0 cm high, 7.0 cm diameter cylindrical quartz vessel with an extraction grid system and an oven containing the fullerene propellant flanged to opposite ends. An RF coil wrapped around the outside of the quartz vessel induces an azimuthal electric AC field inside the chamber. The fullerene plasma is maintained inductively, eliminating the need for hot electrode surfaces inside the discharge chamber. Ignition of the discharge may be obtained by RF breakdown or with the aid of electrons attracted from the neutralizer filament into the discharge chamber by temporarily applying a positive voltage to the screen grid. The RF field further accelerates the electrons inside the discharge chamber, leading to breakdown. Because of the difficulties encountered by Takegahara and Nakayama² in obtaining high wall temperatures, we are investigating the use of graphite yarn around the quartz vessel which can be both inductively heated and resistively heated by an independent power supply.

A small orifice in the side of the effusive cell faces an Inficon model XTM/2 Quartz Crystal Microbalance (QCM) to give real-time flow rate measurements. Prior attempts to monitor flow rate by forming a capacitor with the effusive cell and a C₆₀ dielectric failed because the capacitance change due to thermal effects were of the same order of magnitude as the change due to loss of the C₆₀ dielectric.

The QCM sensor is placed 0.27 m from the quartz effusive cell nozzle. Calibration is performed by monitoring the deposition rate in ng/sec. The fullerene sample is weighed before and after heating to determine the total mass of evaporated material.

Beam diagnostics have thus far been limited to the use of an E x B mass spectrometer which displays peaks of all of the species present in the ion beam. Resolution of large mass ions in this device is not high enough to distinguish between the various fullerenes. This was verified during DC discharge experiments when two peaks corresponding to singly charged and doubly charged fullerenes were observed. No attempt to detect the presence of neutral species was made. Modifications

to the E x B probe are underway to improve resolution in the high mass range. We have also obtained a Beckman IR-18A infrared spectrophotometer which we intend to use for ion beam analysis. The instrument is sensitive in the 4000 to 600 cm⁻¹ range.

The RF ion engine was operated using xenon as the source gas. The thruster was equipped with an optics system consisting of stainless steel screen and accelerator grids. The grids were spaced 1.6 x 10⁻³ m apart and had a set of 19 matching 3.2 x 10⁻³ m diameter holes. They were operated at a total-acceleration voltage of 3.2 kV and a net-accelerating voltage of 1.9 kV.

The discharge could be initiated at a RF power level of 50 W; subsequently, the power could be reduced below 10 W before the plasma would extinguish. Below 40 W, the discharge appeared very dim and no current was extracted from the optics system. Above 40 W, the discharge became considerably brighter and ions were extracted. Figure 10 shows the extracted beam current as a function of RF power when the ion engine was operated at a xenon flow rate of 0.094 mg/s. The beam current increased rapidly with power between 40 and 100 W and then leveled out to a maximum of about 2.9 mA above 100 W.

Further Experiments

If an RF fullerene plasma discharge is demonstrated to be efficient, a less fragile discharge chamber will be required. A thin silicon carbide or alumina vessel may be a viable option.

Chamber wall healing may continue to pose a problem. The difficulty with an inductively heated element around the discharge chamber wall is two-fold; 1) the wall temperature and RF power will be coupled. Optimized performance of the thruster over a range of operating conditions will then become more difficult, and 2) any conducting element will reflect RF power,

The issue of propellant neutralization also has not been adequately addressed. It seems unlikely that hollow cathode neutralizers will be able to operate with a flow of fullerene vapor. Use of a noble gas neutralizer cathode assembly would reduce the system mass benefits associated with using a fullerene ion thruster. In a study of the reaction of C₆₀ with tungsten²⁰, it is noted that because the lowest unoccupied molecular orbital (LUMO) of C₆₀ lies deeper than the Fermi level of noble and transition metals, there is no barrier to charge donation. Hence, negative ion formation of fullerenes in contact with metals may provide a means for C₆₀ thruster neutralization.

Conclusions

We have conducted high temperature stability and material compatibility studies of fullerene mix and pure C₆₀ and C₇₀. At temperatures necessary for fullerene ion thruster operation (873 K), C₆₀ remains stable. However, high temperature

surfaces such as cathodes pose a problem. We have determined an activation energy of 261.5 kJ/mol for the decomposition of fullerene mix in evacuated quartz ampoules. We have constructed an RF thruster to generate a fullerene plasma and to determine the performance of the system relative to noble gas discharges produced in the, same device.

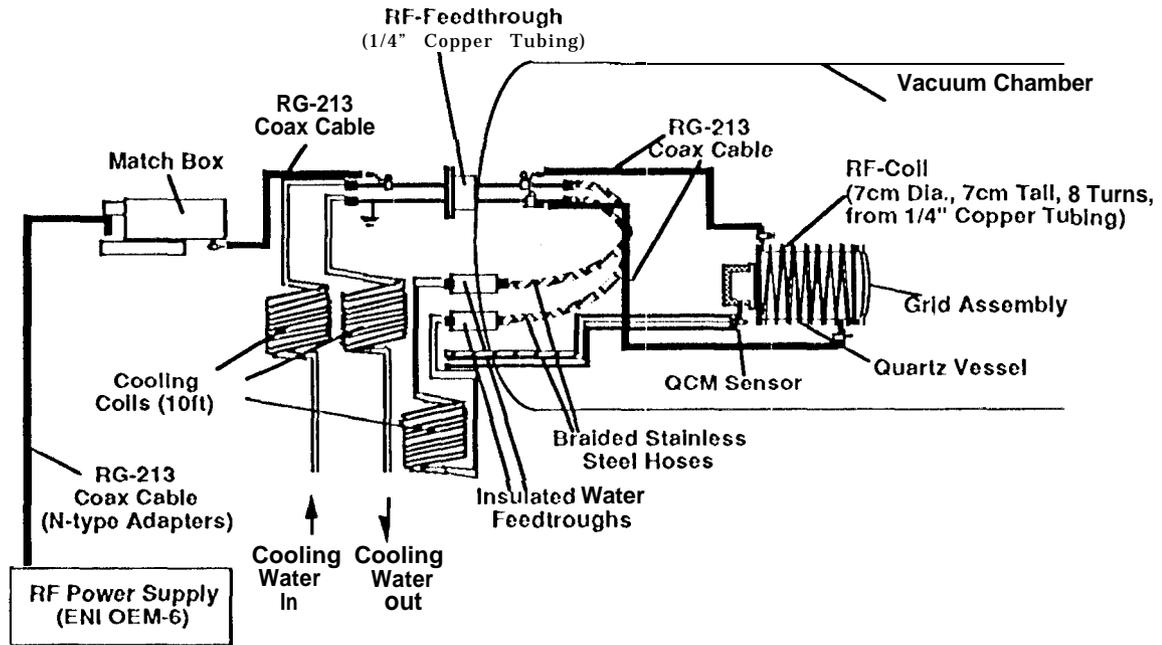


Figure 9. Schematic of the RF thruster assembly.

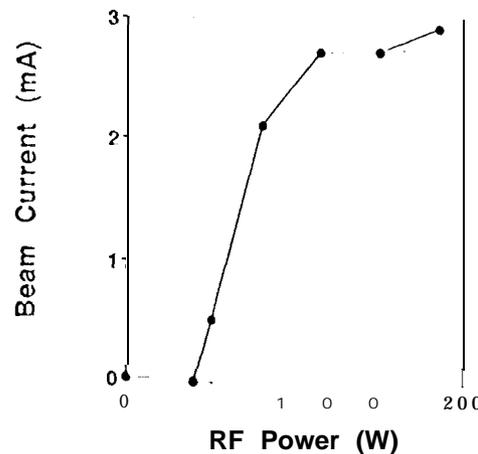


Figure 10, Beam current as a function of RF power for xenon plasma discharge

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