THE PLASMA PRODUCTION OF FULLERENES

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ABSTRACT

The use of plasma technology to dissociate hydrocarbons for the synthesis of fullerenes was explored during this study and led to the development of the *PyroGenesis* process. A plasma reactor, equipped with a non-transferred DC plasma torch, was used to dissociate hydrocarbons. The hydrocarbons investigated include CH_4, C_2H_2, $CBrF_3$, CCl_2F_2 and C_2Cl_4. Best results were obtained with C_2Cl_4.

1.0 INTRODUCTION

Fullerenes, the family of carbon cage molecules, promise to find exciting applications in a variety of areas, including optics, diamond film production, batteries, xerography, electronics and pharmaceuticals (1). Although research in the development of commercial fullerene-based products is actively being pursued, progress in the cost-efficient production of fullerenes is essential to ensure the economic viability of these products. Currently, fullerenes may be produced via the vaporization of graphite rods (2), graphite electrodes (3), carbon black powder (4) or coke (5), the combustion of benzene (6) and the pyrolysis of naphthalene (7). In this paper, we introduce a novel technology based on the thermal plasma dissociation of hydrocarbons to form fullerenes.

2.0 EXPERIMENTAL

Fullerene soot was produced in a spherical reactor (12 in. ID) equipped with a non-transferred DC plasma torch (Fig. 1). Using helium as the inert plasmagas, the plasma torch operated at 35 to 70 kW. The hydrocarbon gas was either mixed with the plasmagas and introduced into the torch, or alternatively, was introduced into the plasma at the torch exit through a nozzle. Hydrocarbons include CH_4, C_2H_2, $CBrF_3$, CCl_2F_2 and C_2Cl_4. The hydrocarbons are dissociated in the plasma, forming a reactive cloud of atoms. By controlling the torch and reactor parameters, some of the carbon atoms recombine to form fullerenes, which condense with soot and other by-products on the water-cooled reactor wall. The gas leaving the reactor then enters the quench zone, a stainless steel receptacle consisting of water-cooled coils, where additional products condense. The reactor system is connected to a vacuum pump, allowing operation from 100 to 760 Torr.

At the end of each run, the reactor was re-pressurized and opened. The soot was collected into pre-weighed containers for extraction and analysis. The fullerenes were extracted by placing a suspension of the soot in toluene into a sonication bath for 30 minutes. The mixture was then filtered to obtain a red-brown solution of extract, which was analyzed by High Performance Liquid Chromatography.

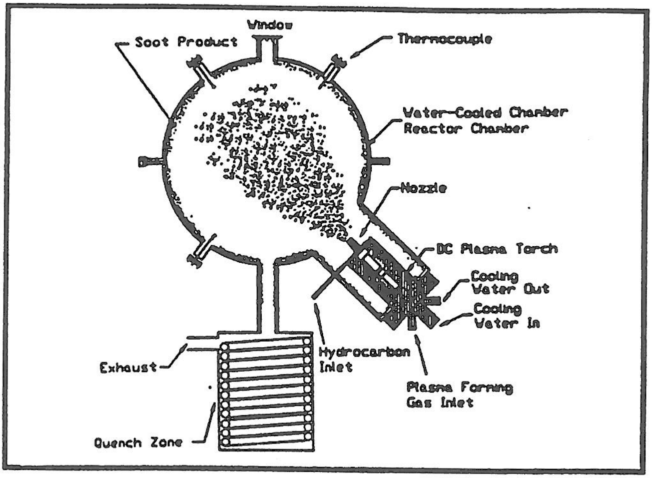

Figure 1: Schematic diagram of *PyroGenesis* reactor system

3.0 RESULTS AND DISCUSSION

3.1 Selection of hydrocarbon

When CH_4 and C_2H_2 were each used as feed materials, the resulting soot did not contain a significant amount of C_{60} (less than 0.05%). Since it was felt that hydrogenated hydrocarbons would not result in high fullerene concentrations, halogenated fullerenes, such as $CBrF_3$ and CCl_2F_2, were investigated. The dissociation of these halogenated hydrocarbons yielded better results, the highest fullerene yield resulting from the dissociation of CCl_2F_2 (0.5 wt% C_{60} in soot).

A thermodynamic analysis, reported elsewhere (8), revealed that both C-H and C-F bonds are stable at temperatures between 2000°C and 3000°C, where fullerenes have been predicted to form (9). C-Cl bonds, however, are not very stable above 1000°C, hence C_2Cl_4 was studied as a feed material.

Using C_2Cl_4 as the feed, the soot pro-duced was richer in fullerenes than in earlier experiments. Mass spectral analysis (Fig. 2), using Fast Atom Bombardment (FAB), indicated that the soot consists of C_{60} and C_{70} (m/z 720 and 840) in addition to C_{76}, C_{78}, C_{84}, C_{90}, and C_{94} (m/z 912, 936, 1008, 1080 and 1128). Our preliminary study, reported herein, focused on the operating consistency of the system, including variations in soot collection and product quality as a function of reaction time and C_2Cl_4 feed rate.

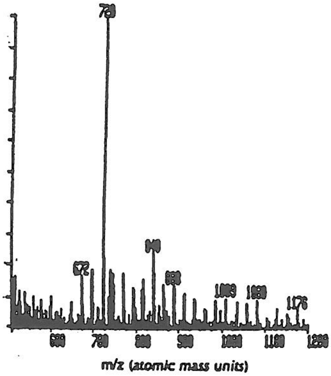

Figure 2: FAB mass spectrum of soot produced via dissociation of C_2Cl_4

3.2 Effect of Reaction Time

For this study, the torch operated at 55 kW with a helium flow rate of 225 l/min and a reactor pressure of 200 Torr.

Fig. 3 shows the effect of reaction time on the reactor temperature. Reaction time measures the total time C_2Cl_4 is fed into the reactor and does not include the time required for plasma ignition and stabilization. Temperatures were measured with K-type thermocouples having a protective ceramic sheath. The thermocouples measured the temperature of the gas near the reactor wall. Due to the insulating properties of the ceramic sheath, the temperature measured serves as a basis for comparison since the true temperature would be higher than the values indicated.

Temperature profiles inside the reactor were obtained for three different conditions: no C_2Cl_4 flow, 0.29 mol/min C_2Cl_4 and 0.44 mol/min C_2Cl_4. When the plasma torch operates under the conditions indicated above, without C_2Cl_4, the temperature near the reactor wall stabilizes at 350°C. However, when C_2Cl_4 is introduced into the plasma, the temperature quickly increases. After 4 minutes, the temperature reaches 580°C and 690°C at 0.29 mol/min and 0.44 mol/min C_2Cl_4 feed rate, respectively. One explanation for this trend is that the soot which deposits on the reactor wall acts as an insulator. Thus, as more soot deposits with time and as a result of higher C_2Cl_4 flows, the temperature inside the chamber continues to increase. It is also possible that the overall energy change, resulting from chemical reactions, is exothermic, thus, contributing to the observed increase in temperature with time.

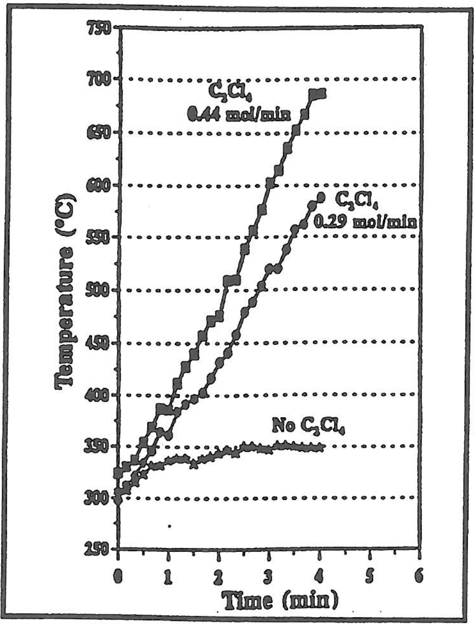

Figure 3: Temperature profile near reactor wall

Under the operating conditions used for this study, the soot collection rate over time was constant. 3.3 g/min of soot was collected on the reactor wall, while an additional 0.6 g/min of soot condensed in the quench zone.

Although the soot collection rate is constant, the C_{60} concentration in the soot decreases with time. The soot collected in the reactor after 2 minutes, contained 3.5 wt% C_{60}, while the concentration dropped to 2.5 wt% after 8 minutes (Fig. 4a). The decrease in the C_{60} concentration in the soot collected in the reactor may be a result of several factors: (i) sublimation of C_{60}, due to increasing reactor temperature with time, (ii) reaction of C_{60} with soot or other by-products during the experiment and/or (iii) decrease in the formation of C_{60} due to the increasing temperature in the reactor.

At 200 Torr, C_{60} begins sublimating at 480°C (10). Thus, it is conceivable that as the reactor temperature increases, C_{60} sublimates and is carried into the quench zone. As a result, there should be an increase in the C_{60} concentration in the soot collected in the quench zone, as is confirmed in Fig. 4a. In Fig. 4b, the overall collection of C_{60} and C_{70} is plotted against reaction time. It is evident that the overall collection of C_{60} decreases with reaction time, however it is difficult at this point to determine whether C_{60} reacts with the other products on the reactor surface or whether the change in temperature of the reactor affects C_{60} formation. The C_{70} concentration in the soot, however, remains fairly constant at 6.3 mg/g, suggesting that C_{70} is less affected by the factors discussed above.

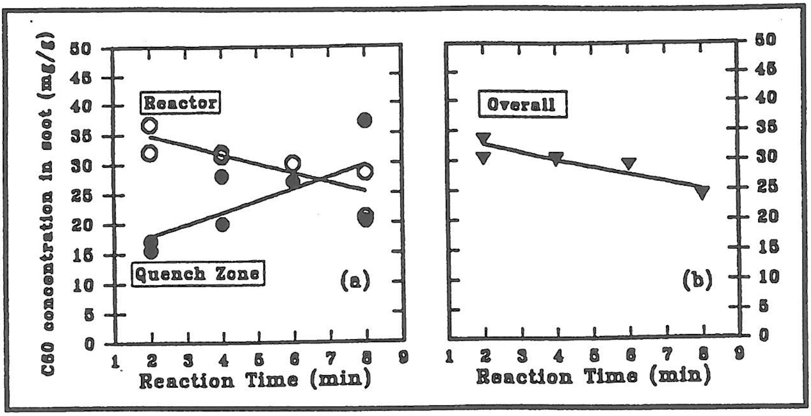

Figure 4: C_{60} concentration in soot as a function of reaction time in (a) reactor and quench zone and (b) overall

3.3 Effect of C_2Cl_4 Feed Rate

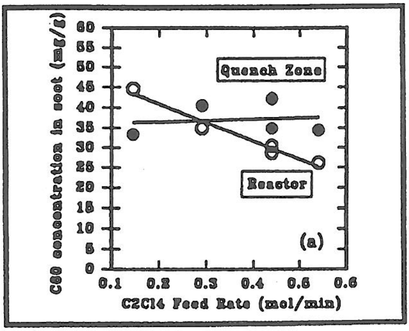

Figure 5: C_{60} concentration in soot as a function of C_2Cl_4 feed rate.

When the C_2Cl_4 feed rate was varied from 0.29 to 0.54 mol/min (65 kW, 225 l/min He and 200 Torr), soot production per mole of C_2Cl_4 was fairly constant at 14.5 g/mol. However, the concentration of C_{60} in the soot decreases with increasing C_2Cl_4 flow rate in the reactor. As seen in Fig. 3, higher flows of C_2Cl_4 result in higher reactor temperatures, which cause losses of C_{60}, primarily due to sublimation. However, in Fig. 5, the concentration of C_{60} in the quench zone does not increase significantly with increasing C_2Cl_4 flow rate, as would be expected if sublimation was the main cause for losses from the reactor. Hence, the ratio of input power to hydrocarbon feedrate is a critical factor, since this greatly affects the temperature of the plasma zone, where fullerenes are expected to form.

3.4 Characteristics of *PyroGenesis* process

The *PyroGenesis* process is capable of producing fullerenes at a significant production rate via the plasma dissociation of C_2Cl_4. With the present lab scale equipment and with a plasma torch operating at 65 kW, the production rate of fullerenes is at least 250 mg/min. A cooler collection zone, using the same power, would result in a production rate of 15 g/hr of fullerenes. Furthermore, since industrial plasma processes can operate at the 1 MW level, as demonstrated by the production of TiO_2 (11) and acetylene (12), fullerene soot production, using thermal plasmas, can be scaled up to produce industrial quantities of fullerenes.

One drawback of the *PyroGenesis* process is that, unlike the soot produced via the vaporization of graphite, the *PyroGenesis* soot contains a variety of chlorinated by-products. These by-products render purification more difficult since chlorinated organic compounds dissolve in similar solvents as those used for fullerenes.

4.0 CONCLUSION

Fullerenes were produced using the novel *PyroGenesis* process, based on the plasma dissociation of halogenated hydrocarbons (C_2Cl_4). It was seen that the collection temperature plays a critical role in the collection rate of fullerenes and consequently, the concentration of fullerenes in the soot. The ratio of C_2Cl_4 feed rate to input power also has an important effect, since this changes the temperature in the plasma. The main advantage of the *PyroGenesis* process, over other fullerene production technologies, is that it can be scaled up to produce industrial quantities of fullerenes.

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