

Hydrocarbon Combustion: A Better Technique for Large Scale Production of Fullerenes.

Mohamed Hammida^a, Antonio Fonseca^a, Paul A. Thiry^b and János B.Nagy^a.

^{a)} **Laboratoire de Résonance Magnétique Nucléaire,**
^{b)} **Laboratoire de Spectroscopie Moléculaire de Surface,**
Facultés Universitaires Notre-Dame de la Paix.
61, rue de Bruxelles, B-5000 Namur, Belgium.
E-mail: mohamed.hammida@fundp.ac.be

Abstract

The fullerenes are a new family of spherical carbon molecules (denoted C_n). They represent the third form of carbon after diamond and graphite. The synthesis of fullerenes in large quantities and at low prices is an industrial and commercial matter of utmost interest. In this study, we demonstrate that the technique of fullerenes synthesis by hydrocarbon combustion in rich mixture is the best technique for the fullerenes production at industrial scale.

In an attempt to optimize fullerenes synthesis by hydrocarbon combustion, we investigated 185 flames by systematically varying all flame parameters such as: pressure, gas velocity, nature and percentage of inert gas, C/O richness and nature of hydrocarbon. Modifying these parameters allowed us to thoroughly analyze the profiles of fullerenes production rate, fullerenes yields ($\%C_n$) in the soot, C_{70}/C_{60} mass ratio and concentration of heavier fullerenes ($C_{n>}$) in flames. These profiles enabled us to completely describe the effect of flame temperature on fullerenes formation by hydrocarbon combustion. These profiles indicate that C_{60} is largely formed in the region where the flame temperature is higher. Another result shows that fullerenes of higher molecular weight (C_{70} , C_{76} , C_{78} , C_{80} , C_{84} , C_{86} and C_{90}) are formed mainly under low flame temperature conditions.

Keywords: Combustion; Flame, Fullerene; Soot, Hydrocarbon, Heavier Fullerene.

Introduction

Since 1990, fullerenes have been available in macroscopic quantities¹; and because of their particular structures, they have continuously attracted the interest of scientists in order to obtain industrial applications. Currently, applications have been developed in various fields: some in materials sciences as superconductors based on fullerenes doped with atoms of alkali and alkaline-earth metals² and as novel optical tool³ and in organic or pharmaceutical chemistry^{4,5} as a new side chain. The biggest obstacles for wide industrial application of fullerenes are presently high cost of production and the difficulty of producing them in large quantity. There is an enormous need to develop techniques that will make it possible to synthesize a broad variety of fullerenes and in quantities necessary for applications at the industrial level and at reasonable cost. Moreover, there is also a need to provide processes able to produce mixtures of fullerenes particularly those rich in C_{70} and in heavier fullerenes where the number of carbon is between 76 and 90, and indicated by $C_{n>}$.

The fullerenes are formed in an inert atmosphere of gas from carbon vapor produced either by laser irradiation^{1,6} or by resistive heating⁷. The possibility that fullerenes can be formed

in soots stemming from flames was proposed previously^{8,9}. The first identification of charged fullerenes, in fuel rich flat acetylene-oxygen and benzene-oxygen flames at low pressure was reported by Gerhardt et al.,^{10,11}. In 1991, the first synthesis of C₆₀ and C₇₀ fullerenes in macroscopic amounts from soot generated in benzene flames was realized by Howard et al.,¹². One major advantage associated with the synthesis of fullerenes in flames results from the ability to control various parameters, such as pressure, temperature, atomic carbon/oxygen (C/O) ratio and initial velocity of the gas mixture at the burner. This allows one to study the process of forming fullerenes in flames and also to follow the evolution of the formation of fullerenes in soot. In this study we investigated the evolution of fullerene formation in benzene-oxygen-argon flat flames as a function of the atomic C/O ratio by varying different flame parameters. The tendency of formation of C₇₀ and heavier fullerene in flames is also discussed.

Experimental Design

The experimental apparatus used for fullerene production is based on hydrocarbon combustion in a rich mixture and has been described in detail elsewhere¹³. The combustion system consists of a flat premixed laminar flame stabilized on a water-cooled burner of 7.5 cm diameter at low pressure. The flames were realized by systematically varying different parameters as: the initial fresh gas velocity at 298 K at the burner between 40 to 50 cm.s⁻¹, the pressure in the combustion chamber between 50 to 100 mbar, the percentage of argon between 0 to 40% and the atomic C/O ratio from 0.7 to 1.35. The flames were stabilized for periods of time varying from 10 minutes to one hour depending on the quantity of soot produced. The soot material, resulting from the incomplete combustion of hydrocarbons produced by the various flames was collected on a filter mounted between the combustion chamber and the vacuum pump and extracted by toluene at higher pressure and higher temperature¹⁴. The extracted solution of toluene was concentrated and analyzed by a High Performance Liquid Chromatography (HPLC) (Waters) system equipped with a diode-array detector. The analytical column (Cosmosil Buckyprep 4.6 i.d. x 250 mm)¹⁵, was used with toluene as mobile phase in gradient elution mode. The flow rate was 1.0 ml/min. and the detection was performed at 330 nm. The volume of the injected solution was 50 µl. In this paper, we present results from 60 benzene - oxygen - argon flames.

Results and Discussions

We discuss successively the effect of inert gas concentration on fullerenes production rate, the evolution of fullerenes yield, of the C₇₀/C₆₀ mass ratio, and of the concentration of heavier fullerenes C_{n>} in soot as a function of the C/O ratio in benzene-oxygen-argon flames.

Effect of Inert Gas Concentration

The results presented in Fig.1a were obtained from benzene/oxygen/argon flames operated at a pressure of 50 mbar and a gas velocity at the burner of 40 cm.s⁻¹. The analysis of the evolution of fullerenes production rate as a function of atomic C/O ratio presented on Fig.1a, enables us to conclude that the presence of argon in the gas mixture is more efficient at small concentration. Indeed, the production of fullerenes in flames is highest at 10% of argon and tends to decrease at high concentrations. The experimental data enable us to highlight two important results. First, the maximum production rate of C_n fullerenes increases by almost 100% at 10% argon and moves towards high C/O values compared to that obtained in pure flames of

C_6H_6/O_2 . This observation confirms the positive contribution of the inert gas to effectively produce large quantities of fullerenes using the combustion process. Second, at high argon concentrations, we observe a net decrease in the quantity of fullerenes formed and also a displacement of the maximum towards low values of C/O ratio (Fig. 1a). This can be explained by a reduction in the efficiency of the combustion process due to a reduction in the initial carbon concentration feed and also to a strong reduction in the temperature of the flame. The highest fullerenes production rate realized in the benzene-oxygen-argon flames is 1292.7 mg/h. This one is obtained at a pressure of 50 mbar and a gas velocity of 45 cm s^{-1} , with a C/O ratio of 1.20 and at 10% Ar concentration.

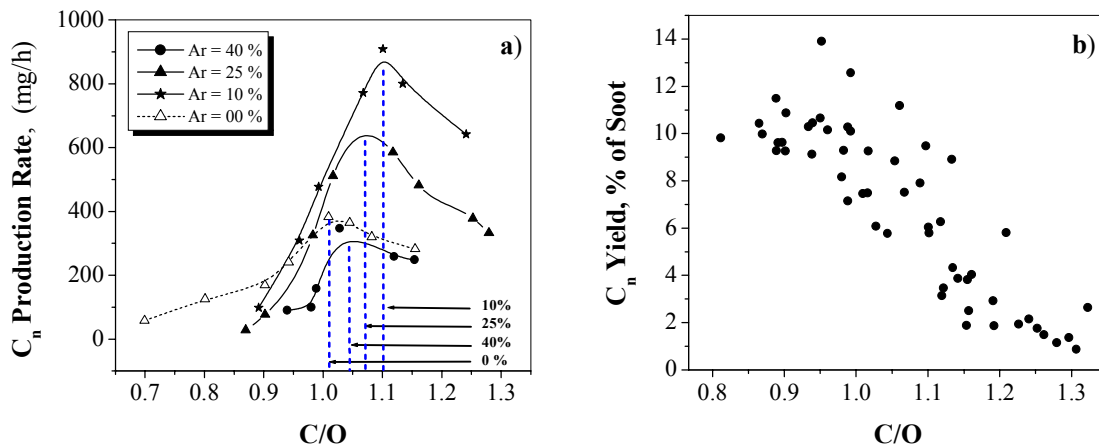


Fig 1: Effect of inert gas concentration on fullerenes C_n production rate (a) and the evolution of fullerenes yield (b) as a function of the atomic C/O ratio.

Evolution of Fullerene Yields in Flames

Another aspect of our research concerns the effect of atomic C/O ratio on the fullerene C_n yields present in the soot of $C_6H_6/O_2/Ar$ flames. Fig.1b gives the % C_n obtained under various sooting flame conditions. This figure reveals that the % C_n reaches very high values and in certain cases achieves a maximum at very low values of C/O ratio. For lean C/O mixtures, the % C_n is included between 8.20 and 13.92. For rich mixtures, we observe a strong reduction in the % C_n as the atomic C/O ratio increases. This means that the maximum yield of fullerenes in flames does not correspond to the maximum production rate of fullerenes.

These results indicate that the process of combustion is very efficient for fullerenes formation at low C/O ratio, before the temperature of the flame reaches very high values. The fact that fullerenes production depends on flame temperature is in agreement with the results obtained by Baum et al.,¹⁶ who observed the presence of a maximum of fullerenes formation as a function of flame temperature. In addition, at low C/O values, precursors of soot and fullerenes, the HAP molecules, are formed inside the flame and the majority of the carbonaceous particles have sufficient time to finish growing and to lead to stable molecules such as fullerenes. The reduction of fullerenes yield observed at C/O ratio ranging between 1.0 and 1.15, where the temperature of the flame is very high, can be explained by a reduction of the residence time of the active particles – precursors of fullerenes – due to the constant position of the burner inside the combustion chamber.

Evolution of C_{70}/C_{60} in Flames

The C_{70}/C_{60} mass ratio for the different flame conditions is in the range of 0.61 - 2.29 compared to 0.02 - 0.18 for the graphite vaporization techniques. The C_{70}/C_{60} mass ratio generated in flames was strongly correlated with the C/O ratio. This is clearly shown in Fig. 2a, where the C_{70}/C_{60} ratio is plotted versus different flames conditions. It shows the presence of a minimum where the flame is hottest. According to these results, we can conclude that the C_{70}/C_{60} ratio is maximum in sooting flame conditions when the temperature of the flame is very low. By comparison with the pure benzene-oxygen flames¹³, the presence of argon in the gas mixture produced soots richer in C_{70} than in C_{60} . The much larger yields of C_{70} and the ability to control the C_{70}/C_{60} ratio by setting the flame conditions is a major advantage of the hydrocarbon combustion technique for the synthesis of fullerenes compared to the graphite vaporization techniques.

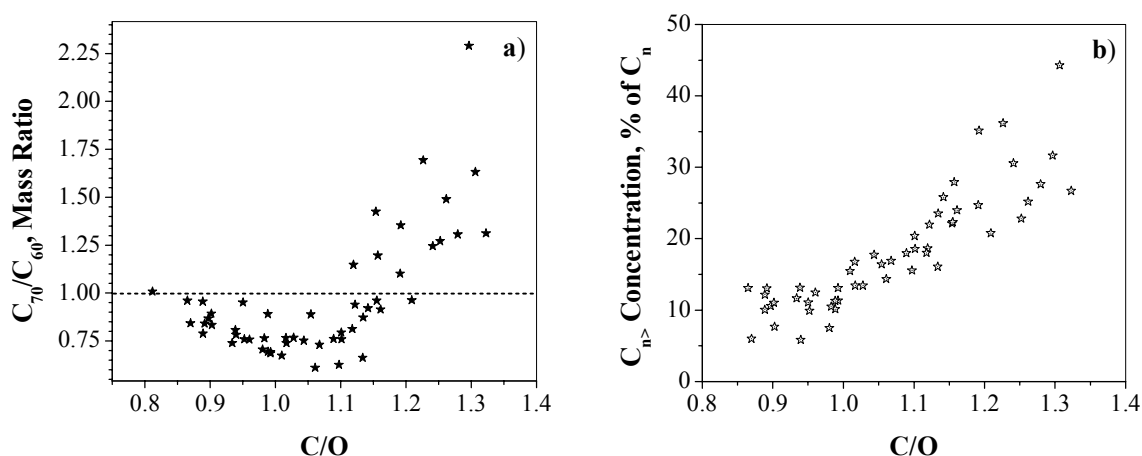


Fig 2: Evolution of fullerenes C_{70}/C_{60} ratio (a) and of the concentration of heavier fullerenes $C_{n>}$ (b) as a function of the atomic C/O ratio.

Evolution of Concentration of Heavier Fullerenes in Flames

The largest concentration of heavier fullerenes ($C_{n>} = C_{76} + C_{78} + C_{84} + C_{86} + C_{90}$) was observed in the low yields and low production rate flames at low pressure (Fig. 2b). Indeed, with weak richness ($C/O \leq 1.0$) where the fullerenes yield in soot is very high, we observe that the concentration of $C_{n>}$ exhibit very low values, lower than 13%. However in the optimal condition of fullerenes production in flames ($1.0 < C/O < 1.15$; Fig. 1a), the $\%C_{n>}$ varied between 13 to 22%. In sooting flame conditions where the fullerenes yield is very weak we observe a strong increase in the concentration of heavier fullerenes in soot. The results of the evolution of the $\%C_{n>}$ presented in Fig.2b indicate that the concentration of heavier fullerenes present in soot is more important when the richness of the gas mixture is very high. The heavier fullerenes ratio obtained with the various flame conditions studied is in the range 5,8 - 44,3% (Fig. 2b). This is largely higher compared to 1 - 2% obtained by the graphite vaporization¹⁷. By comparing these results with those obtained in the study of the evolution of C_{70}/C_{60} mass ratio, we can conclude that the heavy fullerenes, as well as C_{70} , are formed mainly under flame conditions producing large amounts of soot. Thus, the hydrocarbon combustion synthesis of fullerenes at low pressure makes it possible to control the composition of fullerenes soot by means of flame parameters.

This means that hydrocarbon combustion techniques are more efficient than carbon vaporization techniques to synthesize fullerenes for research and for many applications envisioned for the future.

Conclusion

The results of this research clearly demonstrate that hydrocarbon combustion at low pressure can be the best technique for large-scale production of fullerenes. It allows not only the control of the various flame parameters, but also the production of soots richer in C₇₀ and especially in heavier fullerenes with unrivaled concentrations.

Acknowledgements

This research was supported by the Belgian Program on Inter University Attraction Poles initiated by the Belgian State, Prime Minister's Office for Scientific, Technical and Cultural Affairs under contract (OSTC-PAI-IUAP-P4/10) on Reduced Dimensionality, by the EC contract NANOCOMP (HPRN-CT-2000-00037) and by the region of Wallonia SYNATEC (convention n° 0014526).

References

1. Krätschmer, W., Lamb, L.D., Fostiropoulos, K. and Huffman, D.R., *Nature* **347**, 354 (1990).
2. Schon, J. H., Kloc, Ch. And Batlogg, B., *Nature* **408**, 549 (2000).
3. Henari, F.Z., Cazzini, K.H., Weldonand, D.N. and Blau, W.J., *J. Appl. Phys. Lett.* **68**, 619 (1996).
4. Taylor, R. and Walton, D.R.M., *Nature* **363**, 685 (1993).
5. Friedman, S.H., DeCamp, D.L., Sijbesma, R.P., Srdanov, G., Wudl, F. and Kenyon, G.L., *J. Am. Chem. Soc.* **115**, 6506 (1993).
6. Haufler, R.E., Wang, L.-S., Chibante, L.P.F., Jin, C., Conceicao, J., Chai Y. and Smalley, R.E., *Chem. Phys. Lett.* **179**, 449 (1991).
7. Chibante, L.P.F., Thess, A., Alford, J.M., Diener, M.D. and Smalley, R.E., *J. Phys. Chem.* **97**, 8696 (1993).
8. Zhang, Q.L., O'Brien, S.C., Heath, J.R., Liu, Y., Curl, R.F., Kroto, H.W. and Smalley, R.E., *J. Phys. Chem.* **90**, 525 (1986).
9. Kroto, H.W., *Science* **242**, 1139 (1988).
10. Gerhardt, Ph., Löffler, S. and Homann, K. H., *Chem. Phys. Lett.* **137**, 306 (1987).
11. Gerhardt, Ph., Löffler, S. and Homann, K.H., *Twenty Second Symposium (International) on Combustion*, p. 395, The Combustion Institute, Pittsburgh (1989).
12. Howard, J.B, McKinnon, J.T, Makarovsky, Y, Lafleur, A.L and Johnson, M.E., *Nature* **352**, 139 (1991).
13. Hammida, M., Fonseca, A., Doome, R., De Hoffmann, E., Thiry, P.A., and B.Nagy. J., *Twenty seventh Symposium (International) on Combustion*, p. 1663, The Combustion Institute. Pittsburgh (1998).
14. Dayong, S., Ziyang, L., Xinghua, G., Wenguo, Xu. And Shuying, L., *J. Phys. Chem. B* **101**, 3927 (1997).
15. Richter, H., Taghizadeh, K., Grieco, W.L., Lafleur, A.L. and Howard, J.B., *J. Phys. Chem. B* **100**, 19603 (1996).
16. Baum, Th., Löffler, S., Löffler, Ph., Weilmünster, P. and Homann, K.H., *Ber. Bunsenges. Phys. Chem.* **96**, 841 (1992).
17. Smalley, R.E., Haufler, R.E., *Electric arc process for making fullerenes*. United States Patent N° 5,227,038 (1993).