COMPARATIVE ANALYSIS OF SOOTS BASED ON XRD MEASUREMENTS

Árpád Bence Palotás[1] , Renáta Makó [1], István E. Sajó[2]

[1] University of Miskolc, Deparment of Combustion Technology

[2] Chemical Research Center of the Hungarian Academy of Sciences

INTRODUCTION

Environmental protection plays an important role in the life of humanity. Solid particles, especially soots form a large part of air pollutants. Reducing the emission of these materials has a great importance, because they can absorb polycyclic aromatic hydrocarbons that are known to be harmful to human health.

The structure of substances built mostly from carbon atoms are extraordinarily varied from mostly random to a perfectly ordered graphitic structure, which was studied earlier [1-3]. This paper presents the result of another study on soots. The methodology uses X-Ray diffraction measurements which was completed with an evaluation based on Gaussian curve fitting. The project's goal was to search for parameters that exactly determine a given soot specimen in a way that enables one to distinguish a specimen from the others.

MEASUREMENT AND RESULTS

In the course of the experiment ten different types of soots were examined using X-Ray diffraction. Five of them were carbon black made by definite technological processes (N-306, N-373, N-375, N-660, N-772) of Columbian Tiszai Carbon Ltd. at Tiszaújváros, Hungary, two soots were produced by burning candles (G-01, G-02) during a laboratory experiment, two soots were made from Diesel oil (D-01, D-02) collected at the exhaust pipe of a bus, and a graphitized soot made from oil, which was kept at 1600 °C, 1800 °C and 2000 °C for an hour (Grk).

The measurements were carried out using a Philips PW3710/PW1050 X-ray diffractometer operated at 40 kV and 35 mA. The results can be seen in Figure 1.

By examining the figure one can conclude that the diffraction patterns of both the carbon blacks and the soots show similarities in the structure to that of the graphite. Structure of the carbon black specimens is more regular than that of soots, a reason of which can probably be the higher temperature of production.

The interplanar distance values were calculated with the help of the Bragg equation[4]:

$$\lambda = 2d \sin\Theta \qquad (1)$$

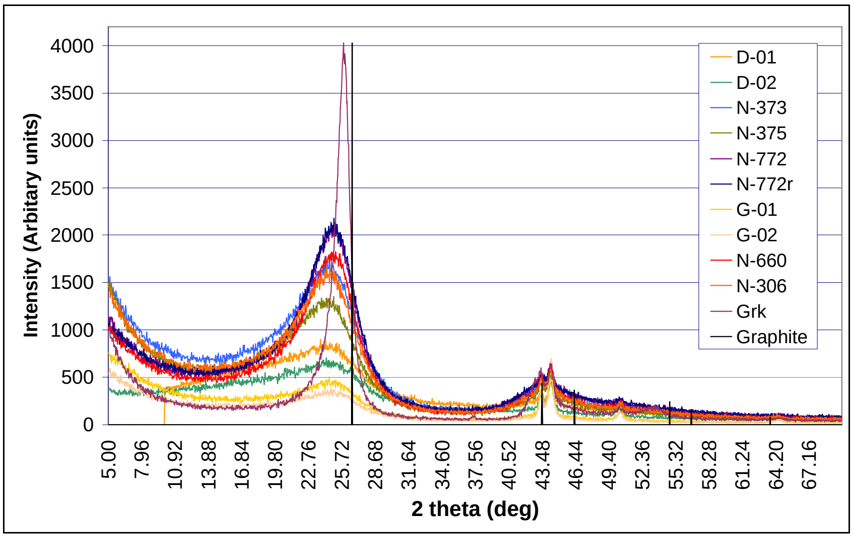

Figure 1
Intensity of carbon black and soot particulates

An important question is the repeatability of the measurements. It is essential to know how precisely fit the diffraction patterns of separate measurements of the same sample. The specimen carbon black N-772 was re-examined in order to get results on the difference in measurements. (Figure 2).

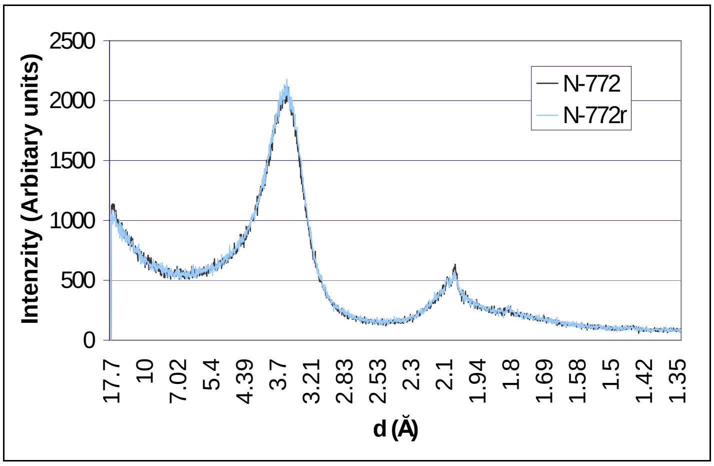

Figure 2
Intensity of carbon black N-772 and reproduction of its measure

The yielding curve of the new sample from carbon black N-772 was designated as N-772r which was obtained using the same instrument and the same wavelength of radiation (λ_{Cu}=1,541862).

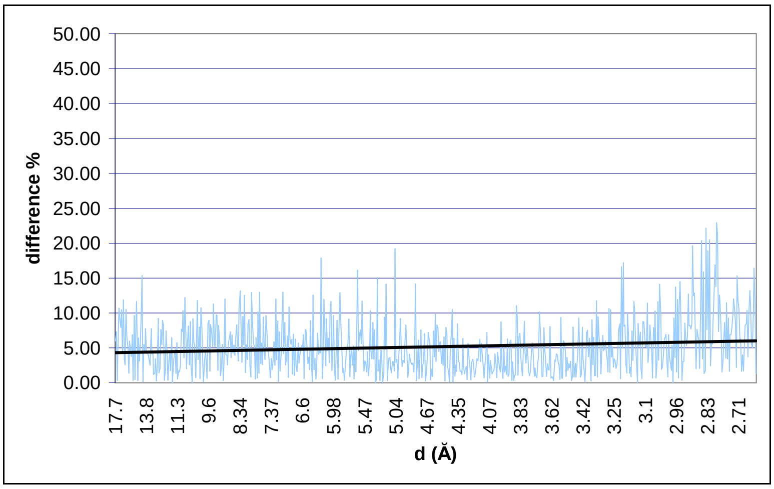

Figure 3
The difference in the diffraction intensity of carbon blacks N-772 and N-772r

Figure 3 illustrates the difference between the results of the two measurements. By examining the figure one can conclude that the divergence around the first peak of the diffraction pattern is about 5%, a value that proves the required repeatability.

EVALUATION

The aim of the evaluation was to find numerical parameters, which can exactly determine the different soot and carbon black patterns. For this purpose the background of every diffraction pattern was separated and a Gaussian curve was fitted to them.

Background separation

Since the first diffraction peak was taken into consideration by Gaussian curve fitting, the other values were dropped. Some points were marked at both end of the peak so that the background curve could be fitted to it with the help of MS Excel. The points of the background curve were calculated to this interval using a logarithmic equation given by the software.

In a next step the background noise designated by the calculated curve was subtracted from the original data values. The resulting curve was already suitable for Gaussian curve fitting although for the search of the optimum fit the curve was smoothed by moving average values (Figure 4).

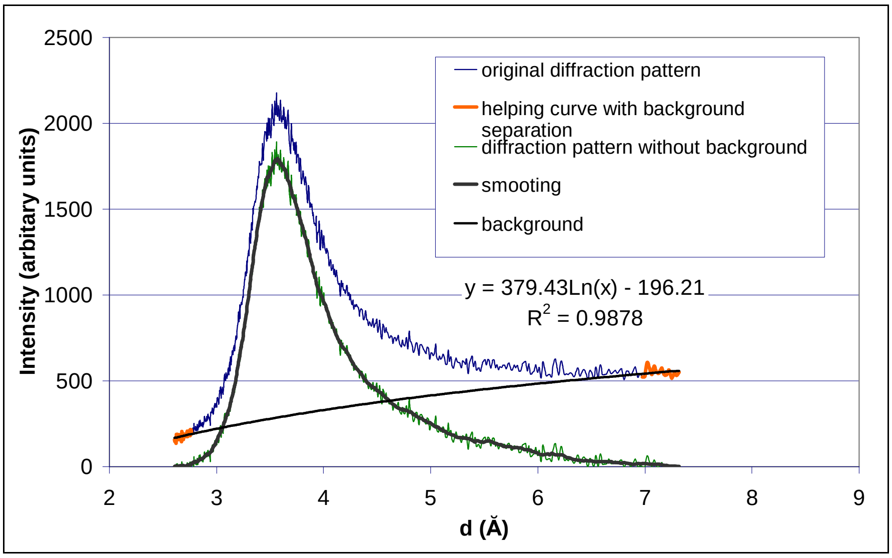

Figure 4
Background separation of diffraction pattern of N-772

Gaussian curve fitting

A software was written to fit Gaussian curves to the first peak of diffraction patterns without background and to find the one which seats the most on the grounds of the following equation [5],[6]:

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{\left[-\frac{(x-m)^2}{2\sigma^2}\right]} \qquad (2)$$

The parameter m signify the maximum point of the curve and σ signify the width of the curve.

A bracket for σ is a user input and during the calculation the software is changing the values of m and σ, fitting the Gaussian curves into it and calculating the value of R^2 according to the following equation:

$$R^2 = \sum_{j=1}^{n} \left(v_{jO} - v_{jG}\right)^2 , \qquad (3)$$

where O means the values of the 'original' curve and G means the values of the Gaussian curve. Finally the Gaussian curve with the least R^2 value is chosen. Figure 5 shows the result of Gaussian curve fitting by the sample of N-772.

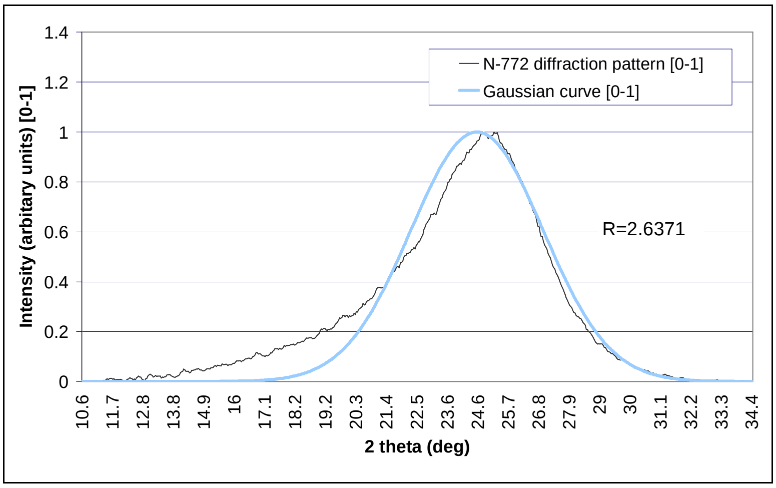

Figure 5
Gaussian curve of the sample N-772

Modified Gaussian curve

This method was refined and a modified form of the Gaussian curve was used to make the fitting more perfect:

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{\left[-\left(\frac{|x-m|}{\sqrt{2}\sigma}\right)^{n}\right]} \tag{4}$$

A new software working on the same principle was made to do this fitting. This way the seating of the curves were better (Figure 6). The values of R^2 are less in case of every pattern.

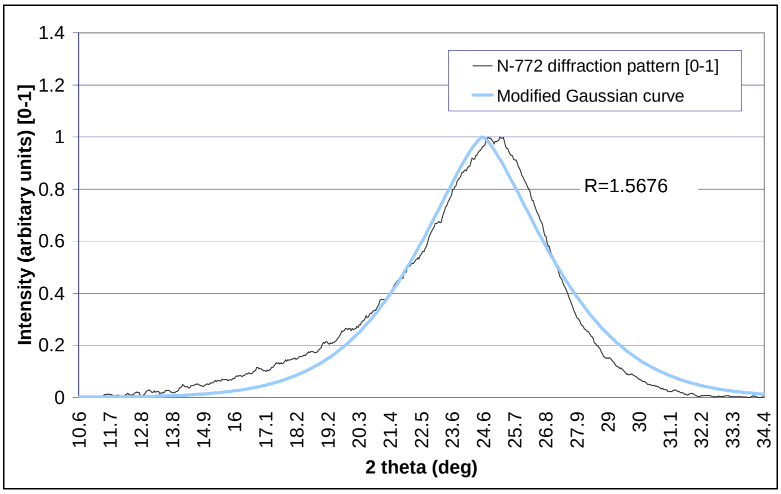

Figure 6
Modified Gaussian curve fitting

CONCLUSION

Three diagrams illustrate the results of the calculation. Figure 7 shows the parameter σ, Figure 8 shows parameter $\boldsymbol{m}$ and Figure 9 shows parameter $\boldsymbol{n}$ for each of the soot and carbon black samples.

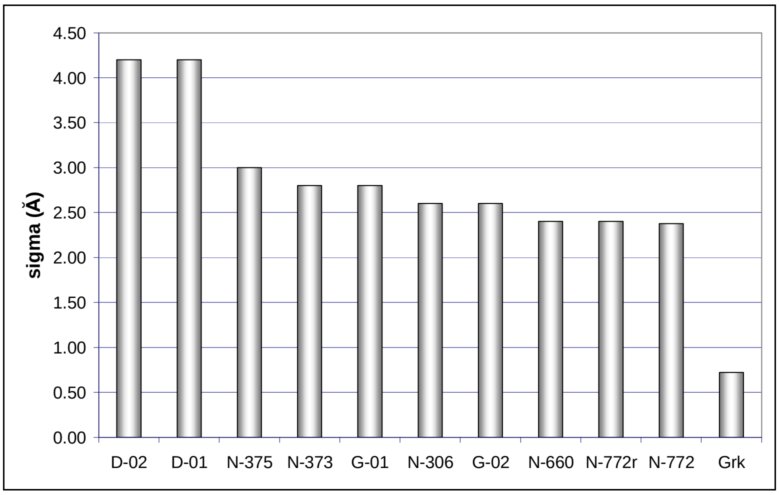

Figure 7
σ values of the samples

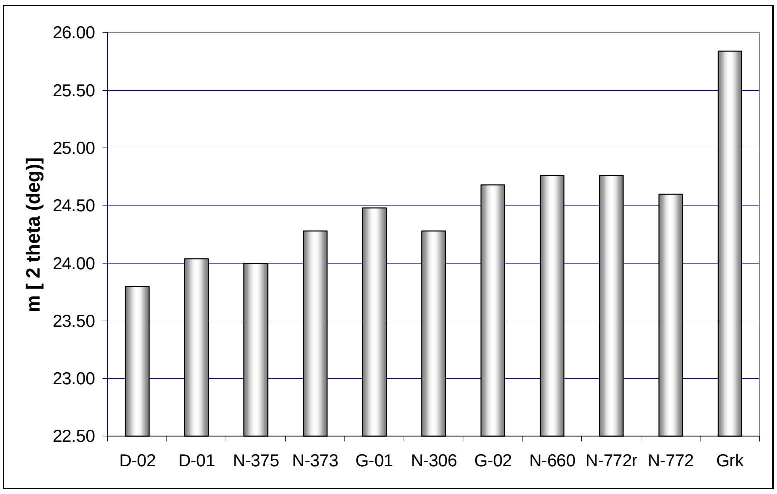

Figure 8
m values of the samples

On the evidence of the counted results it can be seen that there is a substantial difference between the parameters of the graphitized soot and those of the other specimens, a finding that is not surprising, because graphitized soot was formed at high temperature and it was kept there for a long time, for this reason it had time to develop a stricter order.

As for the soots made from diesel oil (D-01, D-02) it can be established that according to their σ parameters they could be separated from the other specimens fairly well.

Having seen the *m* parameters for both of the samples it can be stated that this kind of soot has the most looser structure amongst the examined one, because it's *m* parameter can be found the more farther from that of the of graphitized soot.

Regarding the specimens produced by burning candles (G-01, G-02) it can be seen that on the grounds of their σ and *m* parameters they can be distinguished from the soots made from diesel oil and from the graphitized soot. The average inter-planar distance - under which we mean the value that belongs to the first peak of the curve - was 3.627 Å in case of G-01 and 3.604 Å in case of G-02. This shows that the structure of this type of soot is looser than that of Grk but more ordered than those of D-01 or D-02. All the three parameters of these soots were highly similar, which supports the idea that this evaluation method is usable to separate this kind of soot from the others.

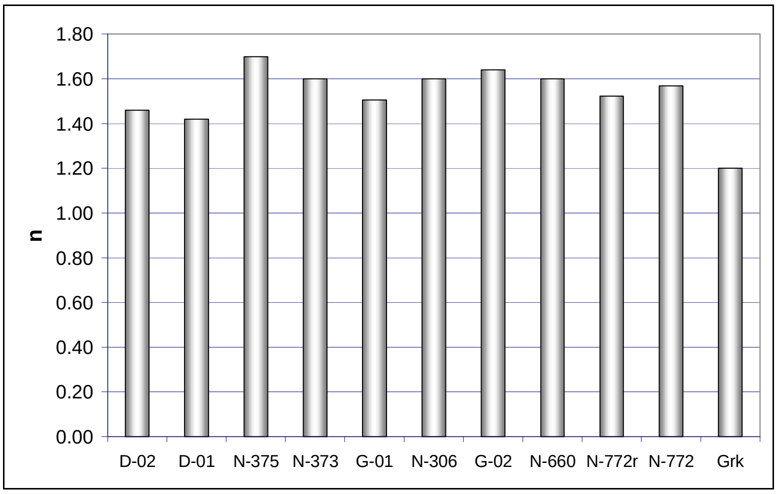

Figure 9
n values of the samples

Considering the carbon black specimens it can be stated that the values are fairly variable. With the help of the three parameters carbon black N-375 and N-772 can be distinguished from the other ones. The first one has the lowest *m* and the highest σ and *n* parameters indicating that it has a more looser structure. The results of the carbon black N-772 on the other hand indicated a different structure. It has the highest *m* and the lowest σ and *n* values consequently the highest order in the structure.

SUMMARY

On the basis of the results of the measurement and evaluating three new parameters have been identified that completes the parameters determining the structure of amorphous carbon with. With their help one can deduce quantified information on the degree of order in the structure of soot or carbon black. This structure is in direct relationship with the circumstances of forming (temperature of forming, annealing time at that temperature, etc).

We would like to continue the developing this method and hope that more information will be known about soot samples originate from an unknown source.

ACKNOWLEDGEMENT

This research is funded by the Hungarian Ministry of Education under the project FKFP 83/2001 as well as by the project OTKA F 035218. Their financial support is greatly appreciated.

REFERENCES

[1] Á. B. Palotás – L. C. Rainey – A. F. Sarofim – J. B. Vander Sande: Soot Morphology: An Application of Image Analysis in High-Resolution Transmission Electron Microscopy
Microscopy Research and Technique 33:266-278 (1996)

[2] T. Ishiguro – Y. F. Suzuki – H. Morimoto: Microstructural Changes of Diesel Soot During oxidation. *Combustion and Flame 85:1-6. (1991)*

[3] Á. B. Palotás – L. C. Rainey – A. F. Sarofim – J. B. Vander Sande – P. Ciambelli: Effect of Oxidation on the Microstructure of Carbon Blacks. *Energy & Fuels. 10: 254-259 (1996)*

[4] P. Bárczy – E. Fuchs:Metallográfia I., Budapest, Tankönyvkiadó, 1981, pp. 76

[5] O. Lukács: Matematikai statisztika, Budapest, Műszaki könyvkiadó, 1996, pp. 41-42

[6] SH atlasz: Matematika, Springer, Budapest,1995, pp. 455