

PLASMA PROCESSING OF ACETYLENE

W. W. Płotczyk

Warsaw University, Department of Chemistry,
Pasteura 1, 02-093 Warszawa, Poland
wwplot@chem.uw.edu.pl

A b s t r a c t. Decomposition of acetylene to carbon black in dc arc plasma argon jet has been investigated. The power of a plasma generator ranged from 5 to 18 kW. It was found that at mean-mass reaction temperature 1270 K the degree of decomposition of acetylene was 96 mol % and product obtained showed a structure suitable for using in a rubber chemistry. The crude carbon black contains small amounts of by-product extractable in organic solvents, as derivatives of acetylene and polyethylene – like polymers. At temperatures exceeding 3000 K the presence of fullerene-like matters was shown.

K e y w o r d s: decomposition of acetylene, plasma, carbon black, fullerene.

INTRODUCTION

The acetylene is one from the raw materials used in the carbon black industry [1,2]. It is an important reactant used especially in a colour ladders coating, printing inks, carbon paper, dry cell as well as rubber chemistry [1,2]. The research concerning the decomposition of acetylene to carbon black in a plasma jet generated both by the high frequency discharge [3] and dc arc plasma jet [4,5] has been growing recently.

Methane [6], benzene [7], kerosene [8] and special oils containing heavy aromatic hydrocarbons [9] were also used as raw materials. In the investigations mentioned above the carbon black was obtained with the properties close to that of an acetylene carbon black, despite of the various kind of the used reactants. The formation of the acetylene black as a result of wide range of the hydrocarbons decomposition at the high temperature can be explained assuming that the process follows the Kassel's [10] sequence schemat. The acetylene is the last gaseous intermediate product of the reaction and then it decomposes to the condensed matter and hydrogen, the final stable products of the hydrocarbon pyrolysis. Dependence on the operating parameters (temperature, reaction time, quench rate) one can obtain, carbon black, coke, graphite and heavy aromatic hydrocarbons.

The aim of this work was to obtain the acetylene carbon black which shows the technical characteristics close to used in the rubber industry as well as evaluate the characteristics of by-products extracted by organic solvents from crude carbon black.

EXPERIMENTAL

The investigations were performed in the plasma reactor which consist of the plasma dc arc generator, the reaction chamber and diaphragm cooling chamber. The flow rate of argon was equal to $2.6 \text{ m}^3\text{h}^{-1}$, while acetylene varied between $0.8\text{--}1.6 \text{ m}^3\text{h}^{-1}$, respectively. The absolute pressure in the reaction chamber was close to 0.105 MPa .

The plasma generator (plasma torch) was connected to copper conus-like reaction chamber. The acetylene was introduced in the direction opposed to the plasma flow through a tube aligned with a reactor axis. The inlet and outlet diameter of reaction chamber was 0.02 and 0.06 m , respectively. Its length was 0.1 m . The solid products of pyrolysis were separated in a system of cyclones and cotton filters.

The mass of crude carbon black obtained in separated experiments varied between 150 and 250 g . The physical and chemical properties and structure of plasma carbon black obtained were examined in according with the requirements of the Polish Standard BN-79/6048. Simultaneously, a part of black carbon was extracted at the boiling temperature of solvents (acetone, hexane, benzene and toluene) by reflux method. The extracts were analysed by spectroscopy methods.

RESULTS AND DISCUSSION

Carbon black synthesis and characteristics

Table contains the results of experiments concerning with preparation of the acetylene carbon black in the plasma jet and, for comparison the physico-chemical characteristics of acetylene carbon black P-1250 and standard carbon black IRB-5.

Table 1. Results of experiments on the preparation of acetylene plasma carbon black.

PARAMETER	1	2	3	IRB-5	P-1250
TR [K] *	1270	1670	2970	-	-
U [MOL.%] **	96	80	78	-	-
SPECIFIC SURFACE [M ² /G] (BY BET)	50	105	101	80	78
IODINE NUMBER [MG I ₂ /G]	39	80	80	82	65
ABSORPTION OF DIBUTYL-PHTHALATE [CM ² /100 G]	186	248	230	131	188

Tr* - mean-mass initial reaction temperature; U** - acetylene to carbon black conversion degree

As shown in Table 1 the high yields of the acetylene carbon black were obtained. The produced carbon black contained over 95 % wt. of elemental carbon black and 1 to 3 % wt. of hydrogen. In the technical IRB-5 carbon black obtained by partial combustion of carbon-related raw material the content of elemental carbon and hydrogen are respectively, 95.2 and 0.6 % by weight.

The carbon black particle shows complex structure with many micro-, meso- and macropores [1,2]. The microporosity of the carbon black is usually determined by BET method based on the liquid nitrogen absorption. As it can be seen from Table 1, the specific surface of the plasma carbon black (determined by BET methods) is similar to that characteristic of a furnace active carbon black (IRB-5) and an acetylene carbon black (P-1250). In the case of the acetylene carbon black from run 2 and 3 the iodine number is higher than the one from run 1. This fact may be related to the high level of mesoporosity of those samples. A relatively large iodine molecule (in comparison with a molecule of nitrogen) can not penetrate into the microporous system of the carbon black. In the case of samples from the runs 2 and 3 the absorption of dibutyl-phthalate (an equivalent of the oil number) was high. This fact may be related to the level of macroporosity of those samples. Absorption of dibutyl-phthalate is used in the rubber industry to measure the structure of carbon black. This structure is a parameter of the behaviour of carbon black in a sample rubber mixture used for rubber manufacturing. In a case of technical carbon black used in the rubber industry the value of absorption ranges usually between 50 and 200 cm³/100 g.

The acetylene carbon black from runs 1, 2 and 3 were tested as the additives in the rubber mix applied for rubber manufacturing. Carbon black from run 3, prepared at a high temperature (2970 K) was found to possess only a little reinforcing ability. It seems that in the case of high temperature pyrolysis of acetylene a high degree of carbon black graphitisation occurs. It results in the formation of numerous micropores which leads to a decrease of the reinforcing ability in spite of a relatively high value of the specific surface obtained by a BET method. Therefore, since the research was aimed at producing a carbon black of high structure appropriate to be used in rubber industry, tests at initial reaction temperatures close to 3000 K were not continued. The carbon black obtained at 1670 K (run 2) showed a medium reinforcing ability.

The carbon black 1 (prepared at a lower reaction temperature) 1270 K showed technological characteristics which was typical for the carbon blacks used in the rubber industry (IRB-5 and P-1250). This carbon black was characterized by the relatively low value absorption of the dibutyl-phthalate).

The investigations of extracts of acetylene carbon blacks

In general crude carbon black contains various kinds of carbonaceous substances [5,7,9,20]. They are usually separated by extraction of carbon black with organic solvents.

The carbon black obtained in the experiment No. 3 originated from quench chamber was extracted with n-hexane for 12 h, next benzene, and then toluene was used as a solvent. The efficiency of the hexane extraction of product from the quench chamber was equal to 4 wt.%. For the carbon black collected from the reaction chamber the yields of 0.5 wt.% were obtained. The extracts were analysed by molecular spectroscopy methods [12].

Figures 1 and 2 show the FT-IR of hexane extracts and ^{13}C NMR spectrum of benzene extracts of carbon black. The extract had intensive orange-red colours.

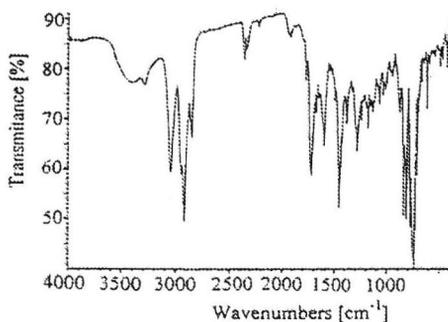


Fig. 1. FT-IR spectrum of hexane extract.

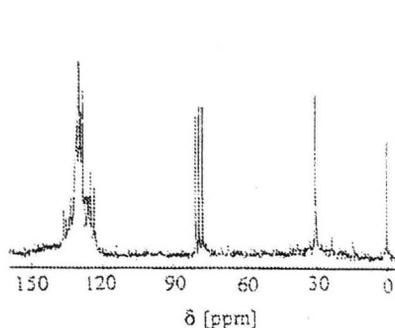


Fig. 2. ^{13}C NMR spectrum of benzene extract.

In the FT-IR spectrum the peaks are attributed to the alkanes. Peaks such as 3030 and 1680 cm^{-1} characteristics for alkenes and 1580 cm^{-1} which exhibit the conjugated band $-\text{C}=\text{C}-$. It is worthy to notice the bands at $2250\text{-}2350$ and 3300 cm^{-1} which are characteristics for substituted polyacetylene-like polymers. It is possible to observe also the bands about 3050 , 1580 and $850\text{-}650\text{ cm}^{-1}$ which are attributed the aromatic compounds.

The ^{13}C NMR spectrum shows bands which are characteristic for CH , CH_2 , CH_3 ($\delta \approx 30$), $-\text{C}\equiv\text{C}-$ ($\delta \approx 78$) as well the aromatic rings ($\delta \approx 130$) and $-\text{C}=\text{C}-$ ($\delta \approx 130$ ppm).

In consequence, the extractable matters are mixtures of polyethylene-like polymers. This conclusion is similar to the reported earlier by Matsumoto et al. [20].

In 1985 Kroto *et al.* [13] discovered, apart from graphite and diamond, the third carbon allotropic form – fullerenes – in carbon vapor resulting from laser

vaporization of graphite. Krätschmer *et al.* [14] found the way to synthesize macroscopic amounts of fullerenes, which gave rise to a period of intensive fullerene research. The results of research studies were presented in review papers e.g. [15]. The basic reactant used for the synthesis of fullerenes is graphite and the most frequently used method of making fullerenes is that of arc discharge between graphite electrodes under reduced pressure.

The synthesis of fullerene in those reactors is carried out at high temperatures, exceeding graphite sublimation point. Huczko *et al.* [16] measured of temperature of such process using spectral methods. The vibration temperature of C_2 radicals was within 5500 K.

Apart from experiments, research is carried out to identify the mechanism of fullerenes synthesis. This includes research work reported by Wilson *et al.* [17]. According to the authors speculations the radicals C_2 , carbon atoms and carbon aggregates C_3 , C_4 ... C_n which are produced in the process of acetylene decomposition in high temperature, play an important part in the initial stages of fullerenes formation. According to Pope *et al.* [18], the presence of C_2H_2 in the mixture of reactants should also promote the synthesis of fullerenes.

As follow from equilibrium calculations made by McKinnon *et al.* [19] for a C-H system, at high temperatures of 2400-2600 K the values of partial pressure of fullerenes become relatively high. For the molecular ratio of C/H=1 at the pressure of 0.1 MPa the concentration of fulleren C_{60} reaches 8 mol %.

As the decomposition of acetylene in the electric discharges plasma jet occurs at high temperatures, and there are C_1 , C_2 , C_3 ... C_n , CH, C_2H and C_2H_2 species available, it seems that fullerenes may be found in the carbon black produced.

This suggestion were confirmed in experiments on the decomposition of acetylene in the plasmas generated by electric discharges [3,20] as well as those with a catalyst [21,22].

It appears from the analysis of paper related to fullerenes synthesis that the process should be carried out at high temperatures. It was also interesting to verify if there are any fullerenes in acetylene carbon black (obtained) at atmospheric pressure. Therefore the supplementary experiments were conducted at high temperatures 2570 (A), 2850 (B) and 3800 (C) K and high argon/acetylene molar ratio: 3, 4 and 6.7 respectively.

Isolation of fullerenes from extractable parts of crude carbon black was carried out following extraction technique [23].

The samples of acetylene carbon black was initially extracted with acetone and further with hexane, next with benzene and finally with toluene. Several miligrams of toluene extracts were obtained in all experiments. 0.01-0.05 wt.% yield in respect to the mass of carbon black was obtained. The UV-VIS and FT-IR spectra are shown in Figs 3 and 4.

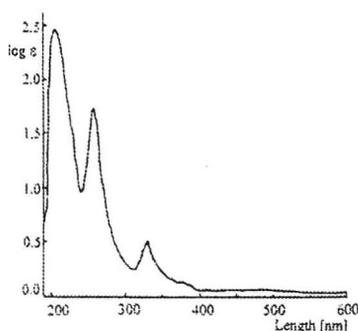


Fig. 3. UV-VIS spectrum of toluene extract.

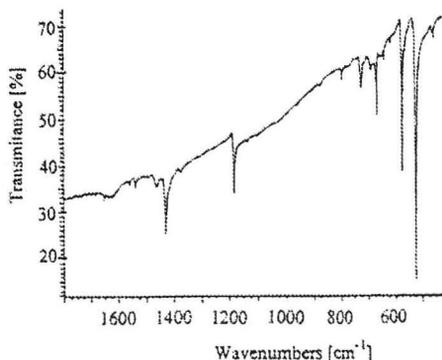


Fig. 4. FT-IR spectrum of toluene extract.

UV-VIS spectrum of extractable product from the third experiment showed absorption peaks of C_{60} fullerene close to those obtained with graphite as the starting material obtained by Ajie *et al.* [24]. FT-IR spectrum toluene carbon black extract from the third experiments pressed in KB pellet matches those obtained by Ajie *et al.* [24] and Krätschmer *et al.* [14].

The presented yields of acetylene fullerenes are lower comparing to those obtained in graphite arcs [15,16] but are comparable to the results by Pope *et al.* [18] which burned benzene in the laminar flow of helium-oxygen mixture.

CONCLUSIONS

The dc arc argon plasma jet seems to be a suitable medium for acetylene decomposition to carbon black. The influence of mean-mass temperature in the range 1270-2970 K on the yield of carbon black, physico-chemical characteristics of the obtained product as well as the contents of by-products contained in crude carbon black was studied. In the process carried out at low temperature (1270 K) obtained carbon black was suitable for using in a rubber industry. It seems that for a high temperature (exceeded 1670 K) the high degree of graphitization of carbon black. The acetylene carbon blacks are characterised by high absorption of dibutylphthalate (186-230 $\text{cm}^3/100 \text{ g}$). The by-products are extractable by organic solvents. The crude carbon black contains to 4 wt % of the by-products. The presence of substituted derivatives of acetylene and polyethylene-like compounds was confirmed by spectroscopic method. The formation of a fullerene-like matter at high temperature of acetylene decomposition was shown, too.

ACKNOWLEDGMENTS

The author wishes to thank Dr hab. inż. Andrzej Huczko for valuable discussion.

REFERENCES

1. **Donnet J.B., Voet A.**, Carbon Black, Ed. Marcel Dekker, New York, 1976.
2. **Voll H., Kleinschmidt P.**, in Ullman's Encyclopedia of Industrial Chemistry, 5th Edition, Exec. Ed W. Gerhart, Weinheim, New York, 5, 140-163, 1986.
3. **Shakourzadeh-Bolouri K., Amoroux J.**, Bull. Soc. Chim. Fr. 2, 189-198, 1986.
4. **Plotczyk W.W., Szymański A., Dull J.**, 9th Int. Symp. on Plasma Chemistry, Pugnochiuso, 671-674, 1989.
5. **Plotczyk W.W., Szymański A.**, 11th Int. Symp. on Plasma Chemistry, Loughborough, 452-457, 1993.
6. **Christofides C., Ibberson V.J.**, 6th Int. Symp. on Plasma Chemistry, Montreal, 254-259, 1983.
7. **Zraževsky W.I., Tertysznyj O.A., Jelcova T.P., Rjabik R.W.**, in Voprosy Khim. i Khim. Techn. 80, 103-107, 1986.
8. **Fulcheri L., Schwob Y., Variot B., Flamant G.** et al., VDI Berichte No 1166, 525-532, 1995.
9. **Idinov N.A., Korolev Ju.M., Polak L.S., Popov V.T.**, Khim. Vys. Energ. 20, 174-180, 1986.
10. **Plotczyk W.W., Szymański A.**, 10th Int. Symp. on Plasma Chemistry, Bochum, vol. 2, Ref. 1.5-13, 1991.
11. **Kassel L.S.**, J. Am. Chem. Soc. 54, 3949-3972, 1932.
12. **Mazurkiewicz R., Rajca A., Salwińska E., Skibiński A., Suwiński J., Zieliński W.**, Metody spektroskopowe i ich zastosowanie do identyfikacji związków organicznych, WNT, Warszawa, 1995.
13. **Kroto H.W., Heath A.W., Brien S.C., Curl R.F., Smalley R.E.**, Nature 318 (1985), 162-164.
14. **Krätschmer W., Lamb D., Fostiropoulos K., Huffman D.R.**, Nature 347, 354-358, 1990.
A. **Huczko A.**, Wiadomości Chemiczne 47, 241-277, 1993.
15. **Lange H., Huczko A., Byszewski P., Ukalski K.**, VDI Berichte No 1166, 325-332, 1995.
16. **Wilson M.A., Pang L.S.K., Willet G.D., Fischer K.J., Dance I.G.**, Carbon 30, 675-693, 1992.
17. **Pope Ch.J., Marr J.A., Howard J.B.**, L. Phys. Chem. 97, 11001-11013, 1993.
18. **McKinnon J.T.**, J. Phys. Chem., 95, 8941-8952, 1991.
19. **Matsumoto O., Ikegami T.**, 11th Int. Symp. on Plasma Chemistry, Loughborough, 1692-1697, 1995.
20. **Jenkins G.W., Holland L.R., Molek H., Fischer J.**, Carbon 36, 1725-1727, 1998.
B. **Couta-Sanchez, Merlo-Sousa L., Huczko A., Soucy G.**, 15th Int Symp. on Plasma Chemistry, Orleans, 610-615, 2001.
21. **Taylor R., Parsons J.P., Arent A.G., Ramorel S.P., John D.T., Aare J.P., Kroto H.W., Walton D.R.M.**, Nature 351, 277-280, 1991.
22. **Aje H., Alvarez M.M., Anz S.J., Beck R.D.** et al., J. Phys. Chem. 94, 8630-8633, 1990.

ROZKŁAD ACETYLENU W PLAZMIE

W. W. Płotczyk

Wydział Chemii, Uniwersytet Warszawski,
Pasteura 1, 02-093 Warszawa, Polska
wwplot@chem.uw.edu.pl

Streszczenie. Badania dotyczą rozkładu acetyleny do sadzy w łuku dc plazmy argonowej. Moc generatora plazmy zmieniano w granicach 5 do 18 kW. Pokazano że przy średniej (mean-mass) temperaturze reakcji 1270 K rozkład acetyleny wynosił 96 mol % a uzyskane produkty posiadają budowę odpowiednią dla przemysłu gumowego. Sadza ma małą zawartość pochodnych acetyleny i polietyleny o charakterze polimerów. W temperaturze powyżej 3000 K stwierdzono obecność związków o charakterze fullerenów.

Słowa kluczowe: rozkład acetyleny, plazma, sadza, fullereny.