The synthesis of different forms of electrically conductive carbon black by the thermo-oxidative pyrolysis of hydrocarbons. Phenomenological and mathematical models of the synthesis process

G.I. Razd’yakonova and V.F. Surovikin

Institute of Hydrocarbon Processing Problems, Siberian Department, Russian Academy of Sciences, Omsk

† Deceased

Selected from International Polymer Science and Technology, 39, No. 12, 2012, reference KR 12/05/24; transl. serial no. 16547

Translated by P. Curtis

Electrically conductive carbon black (ECCB) has been used for 80 years as a filler for composite materials. Of the total volume of ECCB production, 60-70% is used for the production chiefly of cable products, mechanical rubber goods, and plastics [1], the remainder being used in the production of packaging materials for electrically sensitive appliances [2] and chemical current sources [3].

Today, two approaches have been established for ECCB production: in situ directly in the reactor and by surface modification. First came ECCB synthesis in situ (“in the reaction mixture”) from acetylene by the thermal method, and only in connection with the appearance of furnace black grades has the demand for it decreased considerably.

In the first technologies for ECCB production in situ by the furnace method, acetylene was used as the feedstock. To initiate the formation of carbon particle nuclei from acetylene, an aerosol of carbon black was introduced into its gas flow, obtained beforehand at the first stage of its synthesis from liquid hydrocarbon feedstock. Aerosol containing about 1% carbon black ensured a tenfold increase in the mass of acetylene black. Carbon black obtained by this method was similar in volume resistivity \( r_v \approx 0.187 \, \Omega \, \text{cm} \) to acetylene black \( r_v \approx 0.1 \, \Omega \, \text{cm} \), but the low productivity and the explosion hazard of the process resulted in a subsequent search for other technologies.

Developments of alternative technology for the thermo-oxidative pyrolysis of liquid hydrocarbons led to the creation of low-density furnace grades of ECCB of the CF and SCF type. The process of thermo-oxidative pyrolysis of hydrocarbons was characterised by reliability, stability, controllability, and considerably higher productivity. On its basis, a range of conductive grades of carbon back was created, and specific ECCB classifications were established, depending on the aggregate state of the feedstock (from gas or liquid hydrocarbons), the type of process (thermal or thermo-oxidative), and the level of resistivity (low, medium, high). According to the increase in resistivity of composites containing carbon black particles, they are nominally divided into four types (Table 1).

The development of technologies for the thermo-oxidative pyrolysis of hydrocarbons required the creation of multizone reactors for carbon black synthesis [7], in which a high temperature in the reaction zone of about 2100 K was reached by burning a considerable proportion (up to 70%) of the feedstock. The carbon black obtained by this method had a high ash content – up to 10%, which is unacceptable for its conductive properties [8, 9]. However, the production of low-ash-content (less than 150 ppm) and structurally ideal dispersed carbon of high purity is associated with high economic costs, which are not always justified for the consumer [10]. The quality and the manufacturing cost of ECCB are inversely related to one another (Figure 1).

Thus, the established cost of conductive furnace black of the CF type amounts to $US 0.5-1.8 per kilogram, the
The cost of conductive furnace black of the SCF type ranges from $US 2.5 to $US 13.15 per kilogram, and the cost of even lower-density and structurally ideal carbon black of type XCF amounts to $US 19.25 per kilogram [11].

Technological investigations aimed at creating a range of conductive grades of carbon black continue to be urgent, but their considerable labour requirement and at the same time the experience already gained in experiments are stimulating the creation of virtual investigations with the production of models of the process of synthesising different grades of carbon black. However, the available models [12-14] describe inadequately the process of producing conductive carbon black. They do not make it possible to calculate the true residence time of the components in a real industrial apparatus or the degree of completion of the process, which would enable specialist production engineers to choose the optimum production regime with account taken of the technical requirements of the form of ECCB being produced.

The aim of this work, on the basis of experimental investigations and a phenomenological model of the effects occurring during the synthesis of low-density carbon black, was to develop a mathematical model of the control of the technology for synthesising its various classifications.

The construction of the mathematical model began with a formalised description of the system being modelled, using the block principle. According to this principle, the drawing up of the mathematical description is preceded by an analysis of the individual elementary processes taking place in the system being modelled: (1) the production in the reactor of non-porous carbon black particles; (2) their subsequent oxidative treatment.

On the basis of the most general principles, the mechanism of the reactions leading to the synthesis of carbon black is determined by three groups of factors: the composition of the hydrocarbon feedstock and the properties of the product obtained; the temperatures of synthesis and thermo-oxidative treatment; the level of interaction of the oxidant with the medium. Therefore, the variable factors of the process were the degree of aromatisation of the feedstock, the process temperature and the time of contact t of the formed particles with the reaction gases. The responses were the coefficient of surface roughness $K_s$, the degree of structure in terms of the absorption of dibutyl phthalate (DBP), and the volume resistivity $r_v$ of the powder. The time of completion of the process of thermo-oxidative treatment $t$ and the yield of porous carbon black $h_p$ were calculated.

### PHENOMENOLOGICAL MODEL OF THE FORMATION OF LOW-DENSITY CARBON PARTICLES

As a result of the thermo-oxidative pyrolysis of hydrocarbons, carbon black particles with an initial
apparent density of \((1.7-1.9) \times 10^3 \text{ kg/m}^3\), obtained from feedstock hydrocarbons, are burnt up and acquire low apparent density values, \((1.2-1.5) \times 10^3 \text{ kg/m}^3\), in the elastomer medium (Figure 2).

In Figure 2 it can clearly be seen that it is mainly the central regions of the carbon black globules that undergo gasification, while the surface acquires a rough relief, which is caused by its energy inhomogeneity. Thus, during the synthesis of conductive carbon black by the thermo-oxidative method, in addition to change in the porosity of the particles, there is a considerable increase in its roughness coefficient \(K_r\). The relation of \(K_r\) and the porosity of the particles with the process parameters of thermo-oxidative treatment of carbon black was established by the procedure set out by Surovikin et al. [15]. It is expressed by the equation:

\[
K_r = \frac{S_A}{S_g} = 1 + \sqrt[3]{\frac{1.91 \times 10^{-3} \sqrt{2\pi Mr_e^{\frac{2}{3}} RT^{\frac{2}{3}}}}{V(H_2O + CO_2) \times e^{-\frac{24500}{T}} \times \left(\frac{6.02 \times 10^{26}}{N_a} \times \frac{273}{22.4 T} \times \frac{2VO_2}{2VO_2 \times (O_2)} \times \frac{2}{1} \right)^{\frac{2}{3}}}}
\]

where \(S_A\) and \(S_g\) are the specific adsorption and geometric surfaces respectively, \(n\) is the volume occupied by a single carbon atom in a particle (m\(^3\)), \(N_a\) is the number of active impacts of the CO\(_2\), H\(_2\)O, and O\(_2\) oxidiser molecules against the surface of the carbon black particles (m\(^{-2}\) s\(^{-1}\)), \(n\) is the number of active centres per unit surface (m\(^{-2}\)), \(t\) is the time of interaction of oxidiser molecules with the carbon surface (s), \(V_{[H_2O+CO_2]}\) is the volume fraction of H\(_2\)O and CO\(_2\) molecules in the reaction gas, \(V_{[O_2]}\) is the volume fraction of molecules of O\(_2\) in the reaction gas, \(R\) is the universal gas constant (J/K mol), \(T\) is the temperature (K), and \(M\) is the reduced molecular mass of the mixture of gases (CO\(_2\), H\(_2\)O, and O\(_2\)).

Using equation (1), it is possible to calculate the time of completion of the process of heat treatment of carbon black with specified \(K_r\). An example of the results of calculating the times of heat treatment of carbon black with a specified roughness coefficient of \(1.3\) as a function of the process temperature with identical values of the volume fractions of oxygen and carbon dioxide (0.005) and values of the volume fractions of water vapour of 0.12 and 0.20 is shown in Figure 3.

Figure 3 clearly demonstrates the possibility of optimising the temperature of heat treatment of conductive carbon black with specified \(K_r\) by controlling the fraction of oxidising gases \(V_{[H_2O+CO_2]}\).

Increase in \(K_r\) of the carbon black particles is accompanied with loss of carbon black yield according to an equation obtained by Surovikin et al. [15]:

\[
\eta_p = \eta_0 \times \left[1 - \frac{6}{d} \times \frac{V_{[H_2O+CO_2]} + 2V_{[O_2]}}{22.4T} \times 6.02 \times 10^{26} \times \sqrt{\frac{RT \times 10^3}{2\pi Mr_e^{\frac{2}{3}}}} \times \frac{-24500}{T} \times 1^{\frac{2}{3}} \right]
\]

where \(\eta_p\) and \(\eta_0\) are the yield of porous and non-porous carbon black.

The yield of non-porous carbon black can be calculated as the difference between incoming carbon with the feedstock and fuel and the carbon loss with the carbon-containing gases, related to the total feedstock and fuel [16], and is expressed by the following equation:

\[
\eta_0 = 100 \left( G_{\text{fuel}} \times \frac{1}{100} + G_{\text{feed}} \times \frac{79}{N_2} \times \frac{12}{22.4 \times 100} \times \frac{CO_2 + CO + CH_4}{G_{\text{fuel}} + G_{\text{feed}}} \right)
\]

where \(G_{\text{fuel}}\) and \(G_{\text{feed}}\) are the consumption of fuel and feed in the reactor (kg/h), \(C_{\text{fuel}}\) and \(C_{\text{feed}}\) are the carbon content in the fuel and in the feedstock (%), and \(N_2\), CO\(_2\), CO, and CH\(_4\) are the contents of nitrogen, carbon oxides, and methane in the reaction gas (%).

According to experimental data [16], the total content of carbon-containing gases (CO\(_2\) + CO + CH\(_4\)) is connected with \(V_{[O_2]}\) by the linear equation \((R^2 = 0.9837)\)
\[(\text{CO}_2 + \text{CO} + \text{CH}_4) = 23.809 - 94.35 \cdot V_{g/a} \] (4)

The carbon losses with carbon-containing gases are due to the non-stoichiometric ratio of the volumes of fuel gas and air and to the process temperature. In a technological experiment, the dependence of the yield of non-porous carbon black from the same feedstock on the process temperature obeyed a linear equation \(R^2 = 0.9999\):

\[n_b = V_{g/a} \cdot \left(0.9261 \cdot T - 812.98\right)\] (5)

From experimental data, the yield of non-porous carbon black in an isothermal regime depends on the degree of

\[\text{Table 2. Physicochemical indices of the different forms of conductive carbon black obtained by thermo-oxidative breakdown of hydrocarbons and the production process indices}\]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process indices</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t (s)</td>
<td>0.35–0.38</td>
<td>0.33–0.33</td>
<td>0.3–0.4</td>
<td>0.35–0.55</td>
<td>0.3–0.38</td>
<td>0.3–0.4</td>
</tr>
<tr>
<td>hp (%)</td>
<td>43</td>
<td>42</td>
<td>39</td>
<td>39</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td><strong>Main physicochemical properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sext (m²/g)</td>
<td>110–130</td>
<td>105–125</td>
<td>140–160</td>
<td>140–160</td>
<td>140–160</td>
<td>170–220</td>
</tr>
<tr>
<td>SA (m²/g)</td>
<td>170–190</td>
<td>170–190</td>
<td>210–250</td>
<td>210–250</td>
<td>210–250</td>
<td>250–290</td>
</tr>
<tr>
<td>DBP (cm³/100 g)</td>
<td>120–130</td>
<td>130–150</td>
<td>160–180</td>
<td>170–210</td>
<td>170–210</td>
<td>140–160</td>
</tr>
<tr>
<td>r_v (W cm)</td>
<td>≥0.6</td>
<td>≥0.25</td>
<td>≥0.2</td>
<td>≥0.17</td>
<td>≥0.2</td>
<td>≥0.15</td>
</tr>
</tbody>
</table>

Note. T – temperature in the zone of thermo-oxidative treatment; t – duration of thermo-oxidative treatment; hp – yield of porous carbon black; Sext and SA – external and adsorption specific surfaces; DBP – absorption of dibutyl phthalate

\(a\) The designation corresponds to the standard CEV 3766-B2. The properties of the obtained classifications of conductive carbon black correspond to world-analogue types CF (P 366-E, O 367-E) and SCF (P 267-E, P 268-E, P 277-Khit, and P 278-E)

\[\text{Figure 2. Phase contrast micrographs of particles of carbon black before (a) and after (b) thermo-oxidative treatment in the reactor}\]

\[\text{Figure 3. Relationship between the process temperature and the heat treatment time of conductive carbon black with K_r = 1.3 with a volume fraction of water vapour in the gas mixture of 0.12 (1) and 0.2 (2)}\]
aromatisation of the feedstock and can be found from the equation:

$$\eta_0 = \frac{[C/H]}{0.002 + 0.01 \cdot [C/H]}$$

(6)

The influence of the degree of aromatisation of the feedstock on the carbon black yield is due to the reduced activation energy of formation of particle nuclei [16]. When the same feedstock is used, the yield of non-porous carbon black can be optimised by varying the temperature and consumption of the reagents of the oxidative process according to the equation

$$\eta_0 = V_{g/a} \cdot 0.9261 \cdot (T - 812.98)$$

(7)

Under conditions of optimisation of $T$ and $V_{g/a}$, with the use of feedstock with a high degree of aromatisation (correlation index CI or ratio C/H), the concentration of carbon globules in the reactor increases, which promotes an increase in the degree of structure of the product obtained (Figure 4).

In turn, the degree of structure (DBP) of ECCB is a significant factor ensuring conductivity of freely packed particles in the elastomer matrix [8]. It was established in experiments that, with increase in the degree of structure (DBP) and specific surface ($S_A$), the volume resistivity $\rho_v$ ($\Omega \cdot m$) of ECCB powder, measured by the procedure set out in SU 1345104, decreases in accordance with the equation ($R^2 = 0.9004$)

$$\rho_v = 0.0182 \cdot (0.001 \cdot S_A \cdot DBP) - 0.6291$$

(8)

Thus, to ensure a low level of $\rho_v$ and an economically acceptable ECCB yield (35–40%), it is expedient to use highly aromatised feedstock with a CI higher than 140 units.

A mathematical model of control of the process of producing conductive carbon black in general form can be formulated in the form of equations (1) to (8) for mean values.

The obtained system of equations comprises a full stochastic model of the process of producing different forms of conductive carbon black. By solving the model for different technology variants, with the aim of developing recommendations of a technological nature, the most optimum of the variants in terms of the yield of the product and its key properties was chosen. Experimental checking of the variants showed that, in a narrow range of variation of the temperature in the reactor from 1993 to 2223 K, and with account taken of optimisation of the product yield, the key properties of the conductive carbon black differ considerably (Table 2).

On the basis of modelling of the process of producing conductive carbon black by the thermo-oxidative pyrolysis of hydrocarbons and a phenomenological model of the formation of porosity of its particles, a mathematical model of control of its synthesis has been developed and approved, making it possible to assess and optimise the process temperature, the product yield, the contact time of the obtained product in the reaction zone, and the key properties of the product.

It has been shown that the method of thermo-oxidative pyrolysis of hydrocarbons makes it possible to create different forms of conductive carbon black, the ranges of physicochemical and electrical characteristics of which correspond to those of world-analogue furnace black grades CF and SCF.

ACKNOWLEDGEMENT

This work was supported financially by the Russian Federation Ministry of Education and Science (State Contract No. 14.527.12.0024).

REFERENCES

5. http://www.sems.qmul.ac.uk/research/honours/

Received 13.09.2012