Petroleum and Coal

Article **Open Access**

EVALUATION METHOD OF THE GRANULOMETRIC COMPOSITION OF QUINOLINE INSOLUBLE COMPONENTS OF COAL TAR AND PITCH

Fedor F. Cheshko, Evgeny T. Kovalev, Alla Yu. Martynova

Ukrainian State Coal-Chemistry Institute, 61023, Kharkov, 7 Vesnina Str., Ukraine

Received July 19, 2019; Accepted October 10, 2019

Abstract

An evaluation method of the granulometric composition QI of coal tar and pitch has been developed and tested for many years. This method is based on the direct analysis of the tar solution in the quinoline. Tars are used for research after long-term settling from coarse carbon-containing sludge. According to our method, the granulometric composition of QI is determined on a high-precision scanning optical microscope. The distribution by size class is calculated by reducing the number of particles in the field of view of the microscope objective with a stepwise decrease in its resolution. The total content of QI in the tar or pitch is characterized by the number of particles in a fixed volume of the sample. The method allows both to avoid particle size distortions during their separation from raw materials and preparation of the sample, as well as to observe particles without sorbed layers of soluble components.

Keywords: *Coal tar; Electrode pitch; Quinoline insoluble substances; Optical microscope; Granulometric composition; Method of evaluation.*

1. Introduction

As is known, non-boiling products of thermal fractionation of coal tar (pitch) are used in the production of a wide range of conductive materials and structural elements, including as practically no alternative electrode binding materials. They must have optimal binding properties and be well baked with carbon fillers [1]. These materials contain a significant amount of high carbon solid dispersed phase – so called quinoline-insoluble substances (QI). Depending on the production technology and the grade, the content of these components in coal tar and electrode pitch obtained from them can be ~ 1-12 and 4-15% by weight, respectively.

The QI granulometric composition of coal tar is an extremely important indicator that largely determines the physicochemical and technological properties of both the coal tar and the electrode and other binding and impregnating materials obtained from them. For example, it has long been known that, with an equal mass fraction of QI, the higher the viscosity of the pitch is, the higher the dispersion of quinoline-insoluble particles is [2]. However, the data on the size of QI particles, which can be found in the literature, is extremely contradictory. The ranges of particle size fluctuations in them range from 1-2 μm [3] to 0-125 μm [4]. The authors of the work [5] subdivide QI particles of coal tar into the following fractions, μm: <1; 1-3; > 3, and the latter includes no more than 1% by weight of the studied particles. In work [6], it was concluded that the bulk size of QI does not exceed 5-6 μm, but it is noted that when centrifuging coal tar at the stage of industrial cleaning from solid sludge, a noticeable amount of particles with a particle size less than 9-13 μm is released.

The discrepancies between the above results, in our opinion, are explained by the fact that the researchers used QI as the object of study, using one method or another isolated from the original sample. The same situation is observed in the study of coal and other pitchs [7].

Methods for isolating of QI particles are based on filtration (including under pressure), centrifugation, or extraction of the initial tar or pitch. As a result, the precipitations selected are in the form of the dense mass. The resulting precipitate is subjected to dispersion (sometimes

using ultrasound), repeated washing with solvents, and drying. All this cannot but lead to errors in determining the size of particles. For example, it is almost impossible to achieve optimal dispersion of a dense sludge: this stage is characterized by both "undergrinding" and "overgrinding" of the compacted mass. In the authors' opinion, the data obtained as a result of the use of such methods cannot fully represent the true size of the particles under study [6]. An additional reason for this is the complex composition of dispersed QI particles consisting of the particle itself and a layer of substances sorbed on its surface. Among other things, these layers have a significant impact on the interaction of particles with the dispersion medium and with each other. This leads to the formation of stable aggregates of QI particles in the tar mass, they affect the technological properties of the tar and the pitch obtained from it, as a whole, and when QI is selected for research, they are destroyed (at the stage of sludge dispersion), distorting the real picture. Inadequate dispersion of the precipitate before its study leads to reverse distortion.

Another factor that can have a distorting effect on the result of the research is the incomplete extraction (at the corresponding technological stage of industrial processing) from the tar under study with respect to coarse coal and coke sludge. Probably, this leads to the discovery of particles with a particle size of up to 100 μm or more in the composition of substances insoluble in quinoline [8].

2. Experimental

We have developed a method for studying the QI granulometric composition without prior isolation of quinoline insolubles from tars and pitches.

Since a distinctive feature of QI in comparison with other components of coal tar, by definition, is to treat quinoline as a solvent, solutions of tars in quinoline were subjected to research. Microscopy was chosen as the main research method because it allows to visually assessing the state of the sample in the process of determining the indicator of interest. Figures 1-4 show the photographs of the tar solution in quinoline taken with microscopes of various operating principles: in reflected light on an optical microscope (Fig. 1), in the light of a laser beam directed at an angle to the sample plane (Fig. 2), in transmitted light on an optical microscope (Fig. 3).

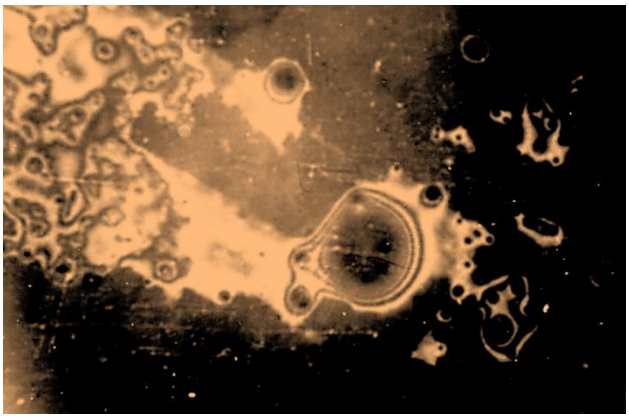

Fig. 1. Micrograph of the solution of coal tar in the quinoline in the reflected light, magnification ×500

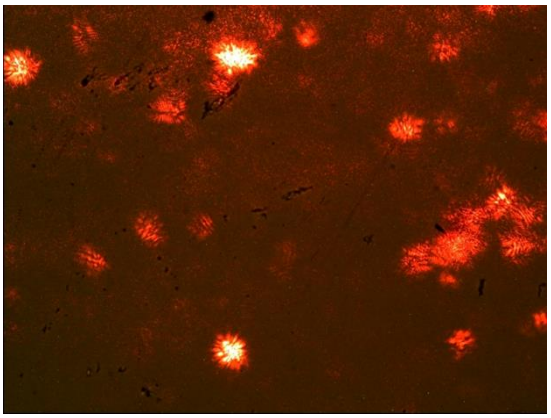

Fig. 2. Micrograph of the solution of coal tar oil in the quinoline in the light of a laser beam directed at an angle to the sample plane, magnification ×500

Reflected light allows to study only the film of the solution, which is characterized by a significant unevenness of the relief and consistency, as well as pronounced effects as a result of sorption phenomena on the surface of particles and in the vicinity of them (probably, some careful analogy with paper chromatography is acceptable here). As a result, the shape and size of particles are distorted (Fig. 1), and it creates problems while preparing the sample for observation and interpretation of the resulting image. In the light of a laser beam directed at

an angle to the sample plane (Fig. 2), distortions are caused by optical effects on the surface relief elements of the particles and on objects approaching the colloidal size of particle size. From the point of view of granulometry, the most acceptable one is the study of the drug in transmitted light, which gives the image of insoluble particles in the form of contrasting projections (Fig. 3).

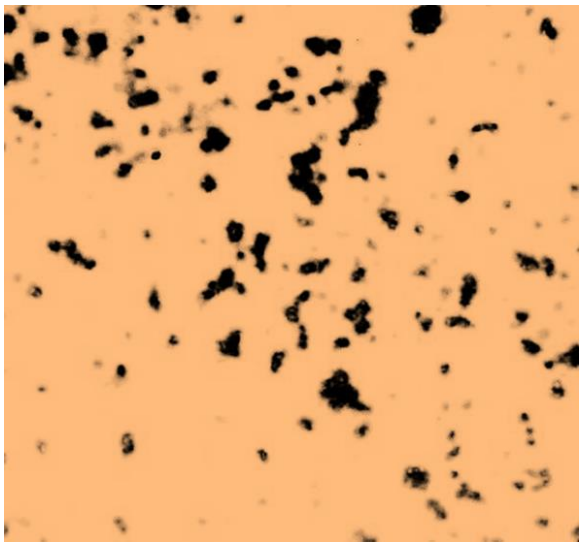

Fig. 3. Micrograph of the solution of coal tar oil in the quinoline in the transmitted light (optical microscope), magnification ×500

The samples for the study were prepared in the form of the tar solution or pitch in quinoline in the ratio of 1:10 by volume. With lower dilution, the solution is not sufficiently transparent, and with a larger particle, it is difficult to fix the particles because of their high mobility.

In order to maintain the purity of the experiment and to ensure the possibility of an approximate estimate of the volume or mass distribution of particles by size class, it is necessary to ensure the constancy of the sample volume under investigation. For this purpose, a drop of solution was placed between two cover glasses. The latter ones were pressed to each other by a specially designed ring clamp, providing a fixed distance between the panes of 10 μm. The excess of the test solution was squeezed out of the glasses. The area of the observed sample was 5×10^4 μm^2 (capture of the microscope objective). Thus, the observed sample volume for all the studied solutions was a cylinder with a volume of 5×10^5 μm^3. The obtained images can be processed using special computer programs, as shown in work [9-10], Fig.4.

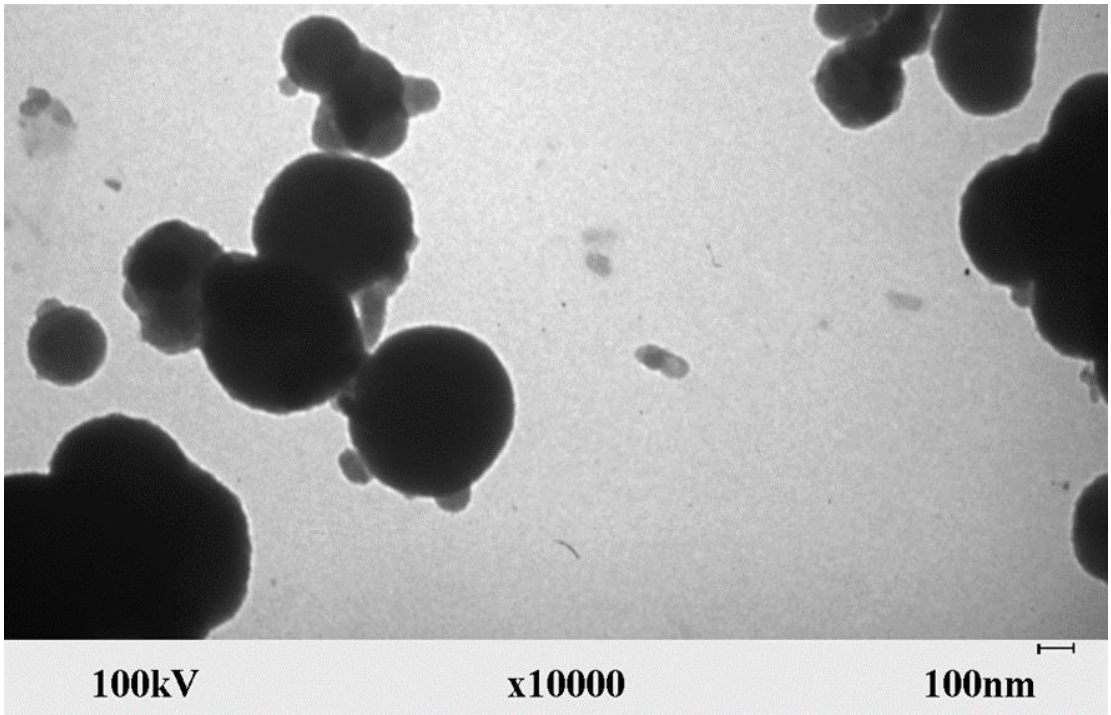

Fig. 4a. Original micrographs of QI

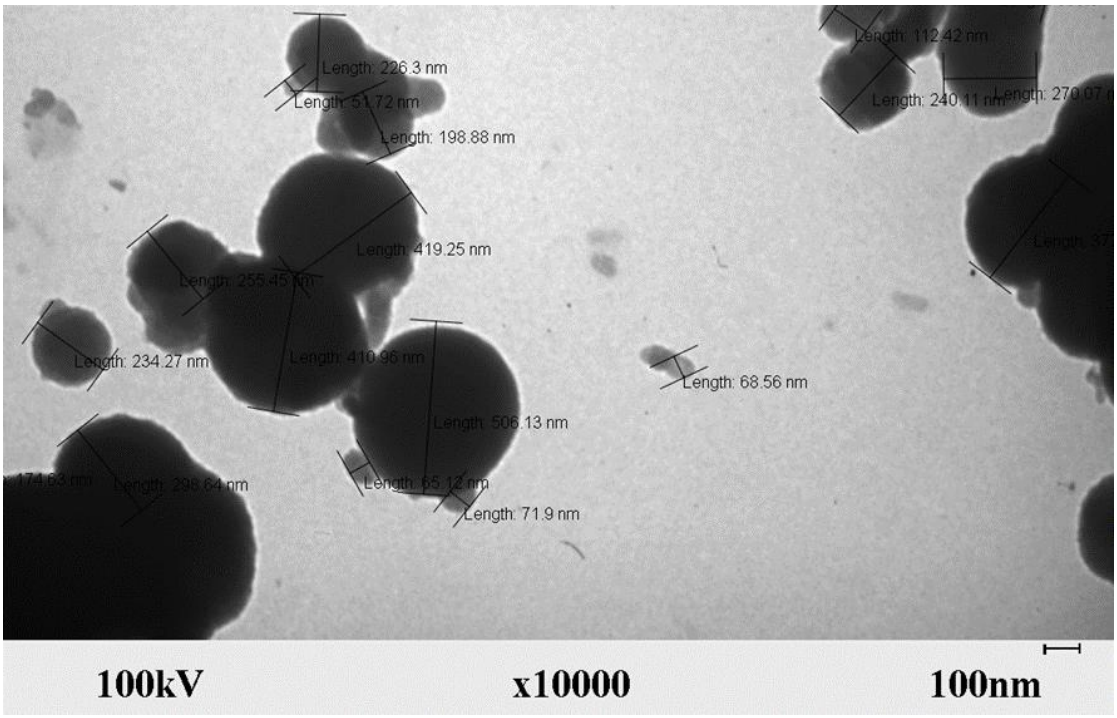

Fig. 4b. Processed micrographs of QI

Fig. 4 shows an example of using such programs for processing photographs obtained when observing in a transmitted light on electron microscope QI particles isolated from coal tar by the filtering method. However, it is preferable to observe the reflected solution of the tar in the quinoline in the transmitted light on an optical microscope. The main feature of the method of research chosen by us lies in the fact that, as revealed in the course of the research, the particles in the solution randomly move under the influence of the Brownian effect and other reasons. This movement is the more intense as, the smaller the particles are and the more dilute the solution is. As a result, to obtain an image of the same high contrast, as in Fig. 4 is quite problematic (see Fig. 3). Some decrease in the image contrast of the projection of the particle also causes the colored layer of the solution between the particle and the sample surface, which causes scattering of the light flux, and it is not constant due to the mobility of the particle. All this, in turn, reduces the accuracy of sizing methods, an example of which is shown in Fig. 4.

To our mind, a more efficient and accurate way is the automatic determination of the number of particles ceasing to be visible with a stepwise decrease in the magnification of the microscope. In this case, the counting of the number of visible particles can be carried out using a specialized electronic device, or by transferring the image to a computer and processing it using a special program. The number of "disappeared" particles is determined by the difference between the results for neighboring multiplicity values.

For example, the principle of operation of the instrument Millipore, which we have used, is the following: at maximum magnification, which allows observing particles with a diameter of fewer than 0.1 μm, the electronic device records the total number of particles in the field of view of the microscope. Then the resolution of the microscope decreases in steps. Particles that disappear from view at every decrease in resolution are in a particular size class.

3. Result and discussion

As an example of using the method developed by us in Fig. 5 shows the distribution curves of QI particles by size for industrial samples of coal tars of various degrees of pyrolysis, the characteristics of which are presented in Table 1 [11].

Table 1. Characteristics of coal tar samples

Number of sample	Density, kg/m^3		Mass content,%	
	of tar	of QI	TI*	QI
1	1215	1418	11.7	6.1
2	1148	1342	6.8	3.3
3	1169	1329	5.4	1.8

** Mass content of toluene insoluble substances*

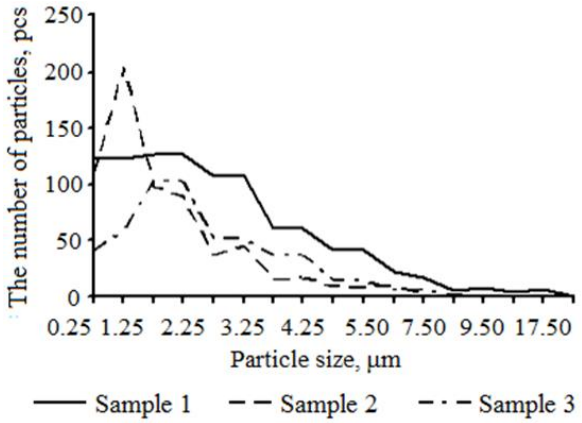

Fig. 5. QI particle size distribution of coal tars

For the study, the samples of tars were selected from the enterprises where the equipment for deslimation effectively worked, i.e., cleaning of raw coal tar from coal and coke sludge, carried by a stream of chemical vapors from the coking chamber and trapped in the tar during its condensation. The density of QI, presented in Table 3, is determined by the pycnometer method from the samples obtained in determining the mass fraction of substances insoluble in the quinoline, using the standard method.

As it can be seen from the above data, the size of QI particles in tars of different degrees of pyrolysis with effective work of the deslimation varies from 0-7 to 0-20 μm. Thus, the number of particles of the solid dispersed phase and their sizes depend on the degree of pyrolysis of coal tar. In this case, what is meant here is dispersed particles, since the sample preparation by dissolving it in the quinoline destroys the sorbed layers. With the efficient operation of the process equipment of the primary deslimation of coal tar in the composition QI, as a rule, there are no particles larger than 20 μm.

Despite the fact that the thickness of the fixed layer during the determinations did not exceed 10 μm, our detection of particles with a particle size up to 20 μm in tars (solutions) is quite understandable. The reason is that large (more than 3 μm) QI particles have an irregular shape. As a result of microscopic studies of solutions of samples 1 and 3, the coefficients of approaching the particle shape to a spherical one were determined: $K = R_{min}/R_{max}$; where R_{min} is the smallest size of the particle projection on the plane, μm; R_{max} – the largest size of the projection of the particle on the plane, μm. For QI particles of tar 1, the value of K ranges from 0.3 to 1.0; for tar 3 – from 0.3 to 0.9.

The data also allows an approximate estimate of the mass distribution of QI particles by size class. To calculate the volume fraction of the particles, you can use the values of the coefficient K, the volume of the microscopic sample, and the degree of dilution of the investigated coal tar with quinoline. To determine the mass fraction of particles of a certain size class, it is possible to extend to all QI particles the density value of the part of QI allocated by the standard definition of the mass fraction of QI. However, such a calculation seems to be approximate and can be recommended not as an absolute characteristic, but only for comparison (with a certain degree of conditionality) of different tars.

4. Conclusion

Thus, from the above mentioned, we can draw the following conclusions:

1. An evaluation method of the granulometric composition QI of coal tar and pitch has been developed and tested for many years. This method is based on the direct analysis of the tar solution in the quinoline.
2. The method allows both to avoid particle size distortions during their separation from raw materials and preparation of the sample, as well as to observe particles without sorbed layers of soluble components.
3. With the efficient operation of the process equipment of primary deslimation of coal tar as a part of the composition QI, as a rule, there are no particles larger than 20 μm.
4. The developed method allows with a fairly high degree of accuracy to obtain information on the proportion of a particular size class as a percentage of the total number of QI particles. With significant assumptions, the results can be converted to volume or mass fractions.

References

[1] Chesko FF, Borisenko AL, Martynova AYu, Shmalko VM, Zelenskii OI. The possibility of reducing the carcinogenicity of coal tar electrode pitches. Pet. Coal, 2018; 60(4): 584-591.
[2] Sannikov AK. Rheological properties of coal tar pitch. Koks i Khimiya, 1990; 4: 15-18.
[4] Romovacek GR. Estimating the concentration of secondary quinoline insolubles. Carbon, 1986; 24 (4): 417-421.
[5] Markov VV, Petropolskaya VM, Batyeva TS, Semenko LE, Dedikov SI, Sibirko VP, Storozhenko OT. About the obtaining of coal tar with a low content of quinoline insoluble substances. Koks i Khimiya, 1984; 8: 31-36 (In Russian).
[6] Baoquan Z. Achieving good-quality tar at Hamilton works. Proceedings of the Iron & Steel Technology Conference, 2009; 1 (A): 79-88.
[7] Mukina NV, Bannikov LP, Cheshko FF, Achkasova GG. The influence of the particle size distribution of the solid dispersed phase of coal tar on the efficiency of its separation in a continuous centrifuge. Journal of Coal Chemistry, 2012; 1-2: 34-43.
[8] Zhu Ya-ming; Zhao Xue-fei; Gao Li-juan; Jun Lv, Cheng Jun-xia; Lai Shi-quan. Properties and micro-morphology of primary quinoline insoluble and mesocarbon microbeads. Journal of Materials Science, 2016; 51(17): 8098-8107.
[9] Cheshko F. Microscopic study of the coal tar carbonaceous dispersed phase. Chemistry & Chemical Technology, 2011; 5(3): 355-362.
[10] Cheshko FF. Complex microscopy of the primary component of quinoline insoluble substances. Journal of Coal Chemistry, 2013; 4: 59-69.
[11] Kovalev ET, Pityulin IN, Cheshko FF. Handbook of coke-chemist. V. 3. Capture and processing of coking chemical products. Part 14. Processing of coal tar; Publishing House "INZHEK": Kharkov, 2009; p 432.

To whom correspondence should be addressed: Dr. Fedor F. Cheshko, Ukrainian State Coal-Chemistry Institute, 61023, Kharkov, 7 Vesnina str., Ukraine, E-mail chishkof@ukr.net