Testing the reduction properties of coke produced from a mixture of hard coal and rubber wastes

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Abstract. The article presents the method of utilization of rubber waste consisting in the production of coke from a mixture of hard coal and rubber waste from ground tires. In the coke obtained this way, the properties of the coal and rubber mixture were tested, the following indices were determined: reduction properties - CRI and coke strength after the reaction test - CRS.

1. Introduction
Reduction of wastes volume is the main objective of wastes’ management. 1991/31/EC Directive, which is in force in EU countries, requires reduction of waste components, which are biodegradable, respectively to the following levels:

- by 25% in 2010 in relation to the level in 1995,
- by 50% in 2013 in relation to the level in 1995,
- by 65% in 2020 in relation to the level in 1995.
The diagram (figure 1) presents the utilization of rubber wastes from used car tyres in EU countries in 1997, 2002 and 2006. It clearly shows that within last ten years not utilized wastes (1997 - 71%) were used in much greater amount for power purposes (2006 - 60%).

Recently a series of trials solving a problem, important for the present economy, i.e. rubber wastes’ management by their pyrolytic degradation, have been undertaken.

Rubber wastes from car tyres can be used in technological processes, such as production of electric power and heat, or in processes of cement production and metallurgical processes.

It is also known that rubber has reduction properties [2, 3] and can be used for technological processes as a substitute for coke.

The main tests objective was to determine an optimal percentage of coke or coal substitution by rubber for technological use.

Table 1. Production of hard coal and coke in Poland within 1995÷2005 [4].

| Specification       | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 |
|---------------------|------|------|------|------|------|------|------|------|------|------|------|
| Hard coal production, mio ton | 137  | 138  | 137  | 116  | 112  | 103  | 104  | 104  | 103  | 100  | 97.9 |
| Coke production, mio ton       | 11.6 | 10.3 | 10.5 | 9.8  | 8.5  | 9.1  | 9.0  | 8.8  | 10.2 | 10.2 | 8.5  |

In Poland about 10 mio. tons of coke (table 1) is produced per year. Almost 12 mio. tons of coal must be coked in coking plants to produce such amount of coke. The process for rubber wastes utilization of by using them in a form of admixtures (of up to 5% of weight) in a coked coal enabled to eliminate up to 600 thousand tons of wastes per year.

The objects in which such processes take place have suitable technical equipment that enables to carry out the processes according to the requirements of environment protection law.

Diminution of degradation of natural environment by reducing the production of minerals and minimization of nuisance of wastes as regards natural environment, by limiting the surface area of their disposal, is a benefit, which results from combustion of coke with rubber wastes. Cheap and
simple process of grinding, separation and coking technology is a condition for the process profitability.

Coke is commonly used in metallurgical, cement and power processes.

Coke is a fuel, which is obtained by keeping the hard coal in a temperature 600-1200°C in a specially designed coke furnace, which uses off gases (without a presence of oxygen). It has higher calorific value than typical fossil coal because it includes at least 90-95% of pure coal element. However, special sorts of coal, at a suitable technology, can give coke of purity even up to 98%. Gases, liquids, inflammable substances (e.g. sulphur) and other substances (mainly organic substances), which are degradable in such temperatures, are removed from raw coal in a coking process [5].

2. Laboratory tests
The properties of coked coal and rubber mixture, which are the subject of this paper, were tested at the Measurement-and-Research Central Laboratory in Jastrzębie Zdrój, Poland.

CRI and CSR indices, applied for assessment of quality of industrial cokes used in metallurgical industry, were used to determine the properties of coked mixture (NSC test).

2.1. CRI (coke reactivity index)
CRI characterizes reactivity of coke towards carbon dioxide, i.e. its reduction properties. It can be determined on the basis of coke mass loss during its reaction with carbon dioxide in a temperature 1100 °C within 2 hours (figure 2).

![Figure 2. Retort fed with coke just after determination of CRI [6].](image)

2.2. CSR (coke strength after reaction) index
This index characterizes changes of coke strength after reaction. Its value is determined after determination of percentage mass content of grains of size bigger than 10 mm, which remain after mechanical working of sample of gasified coke in a device for barrelling (figure 3).
Figure 3. Device for barrelling of coke sample after testing the reactivity [6].

2.3. Test stand
RF-33/KK device (figure 4), for determination of coke reactivity index (CRI) towards carbon dioxide, consists of three main components: electric furnace consisting of two symmetrical halves, which touch themselves in a vertical plane, together with a set of retorts, of a precise scale as well as of a computer station, which controls all the system (figure 5).

Figure 4. Test stand for determination of coke reactivity index (CRI) towards carbon dioxide [6].
3. Preparation of samples
Coal was pre-ground in a worm mill and then sieved on a mechanical screen to the grain size of 3-0 mm. Broken rubber from the tyres was sieved to the grain size of 2.5-0.5 mm.

Then the mixtures of hard coal and rubber were prepared according to table 2 and ten 5 kg-samples were prepared from the mixture.

The samples, after dividing into five parts, were poured to the retort in portions; a special bar rammed the layer to obtain approximately the same density. A density of layer was assessed by monitoring the depth of rammer bar indentation in a retort.

3.1. Coking of mixture (feed)
Retort with feed was put into a cold furnace and after bringing the walls closer to retort their intensive warming up started. After about 20 minutes the furnace walls reached a temperature of about 600°C, and after 80 minutes a temperature of 850°C. The temperature inside the feed was constantly controlled during coking. When a formed coke solid reached in its middle part a temperature of 950°C, what happened after 160-180 minutes from the beginning of warming up of retort, a coking process was stopped and the retort was taken out of the furnace. Then the nitrogen passed through the retort at a flow rate 10 l/min till the moment when coke reached a room temperature.

3.2. Testing method
Preparation of analytical coke sample for tests and determination of CRI and CSR indices were conducted according to a standardized method [7].

3.3. Determination of measuring points
Samples of content given in table 2, which meet the requirements of experiment and guarantee the best representativeness of results of conducted analysis, were prepared for tests. Below measuring points correspond to roots of Chebyshev’s polynomial.

5 measuring points were initially assumed, and maximal and minimal values were additionally measured.
Masses of coal and rubber for each measuring point were presented in table 1. Measurement No. 3, as a mean value, was repeated 4 times for statistical analysis.

Table 2. Distribution of measuring points with the use of Chebyshev’s polynomials and assumed minimal and maximal values [6].

| Measuring point | \( x_k = \cos \left( \frac{2 \cdot j - 1}{2 \cdot k} \cdot \pi \right) \) | Rubber content \( Z_g(\%) \) | Coal (kg) | Rubber (kg) |
|-----------------|-------------------------------------------------|------------------------|-----------|-------------|
| max             | 1.00000                                         | 10.00                  | 4.5000    | 0.5000      |
| 1               | 0.95106                                         | 9.75                   | 4.5122    | 0.4878      |
| 2               | 0.58779                                         | 7.93                   | 4.6031    | 0.3969      |
| 3               | 0.00000                                         | 5.00                   | 4.7500    | 0.2500      |
| 4               | -0.58779                                        | 2.06                   | 4.8969    | 0.1031      |
| 5               | -0.95106                                        | 0.24                   | 4.9878    | 0.0122      |
| min             | -1.00000                                        | 0.00                   | 5.0000    | 0.0000      |

4. Results

The first tests for power coal were not successful as the mixture of power coal and rubber gave loose coke, which was not suitable for testing the reduction properties.

Figure 6. Sample, which was not suitable for determination of reactivity index [6].

Thus, coke coal of 35 type from “Zofiówka” Colliery of the following parameters: ash content \( A_d = 7.07\% \), total water content \( W_t = 10.0\% \), volatile compounds \( V_{daf} = 24.4\% \), was used in the next tests.

This coal enabled coking of coal-and-rubber mixture and in the whole range from 0 to 10\% of rubber admixture it did not show a tendency to crushing (figure 6).
A sample of coke, which was formed of coal with 5% of rubber admixture, is presented in figure 7. Darker spots are the coked rubber.

Table 3. Results for measuring points with the use of Chebyshev’s polynomials and assumed minimal and maximal values [6].

| Measurement | rubber content (%) | CRI (%) | CRS (%) |
|-------------|--------------------|---------|---------|
| 1           | 0                  | 31.8    | 56.8    |
| 2           | 0.24               | 31.6    | 58.3    |
| 3           | 2.06               | 33.4    | 58.2    |
| 4           | 5                  | 34.1    | 54.6    |
| 5           | 7.93               | 35.7    | 48.5    |
| 6           | 9.75               | 37.3    | 41.1    |
| 7           | 10                 | 37.9    | 40.5    |

Figure 8. Results of CRI and CRS indices for mixtures of hard coal with rubber admixture from 0 to 10% [6].
5. Conclusions
Results of measurements show that reduction properties of coke increase with increase of rubber admixture, but coke strength decreases. This phenomenon is described by the following equations [6]:

- reduction properties of coke: \( \text{CRI} = 0.0242g_{E}^{2} + 0.3481g_{E} + 31.867 \)
- coke strength \( \text{CRS} = -0.279g_{E}^{2} + 0.9897g_{E} + 57.353 \)

The test on superposition could not be conducted due to difficulties in CRI and CRS results for pure rubber, because it could lead to the failure of RF-33/KK device.

The use of rubber waste as fuel for production of coke limits degradation of natural environment by a decrease of output of minerals.

During combustion of coke, which contains rubber, i.e. increased amount of chlorine (action of microcomponents), it is emitted again (reemitted) in the amount, which mainly depends on conditions of combustion process.

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