Polish coal tar resource base for the production of coal tar pitch for the electrode industry

Zbigniew Robak, Teresa Topolnicka
Scope of presentation

1. Introduction
2. Properties of coal tar produced in Polish coking plant
3. Basic properties of coal tar pitches for electrode industry
4. Advanced method of physicochemical characterisation of pitches
5. Summary and conclusions
About high temperature coal tars

Tars are liquid or semisolid products obtained by thermal decomposition of natural organic material – coking coal.

Properties and composition of tars and pitches depend not only on the raw material but also on the temperature conditions during thermal treatments.

High temperature coal tars are generated by coking of coal in temperature range between 1000 - 1300°C and consist of stable aromatics.

Every year in Poland approximately 400 – 500 thousand ton coal tar is produced mainly in the form of high temperature tars as a by-product of foundry, blast-furnace and industrial – domestic coke production.
Industrial importance

**ArcelorMittal Poland’s** Zdzieszowice Division is not only the biggest, but also one of the most modern coke plants in Europe. Production capacity of 4 new coke batteries introduced between 2003 and 2008 comes to 3 million tonnes of coke a year. The **Kraków Division** which was brought to life in 1954 now is a flagship steelworks plant of ArcelorMittal Poland.

**Coke Plant Przyjaźń S.A.** started production in 1987, when first coke was pushed from battery #1. The millionth tonne of coke was produced on 1988.
Polish coking plants

- Coke plant Zdzieszowice of ArcelorMittal Poland S.A.
- Coke plant "Walbrzych"
- Kombinat Koksochemiczny "Zabrze" (Coke plant "Jadwiga")
- Kombinat Koksochemiczny "Zabrze" (Coke plant "Przyjazn")
- Coke plant in Kraków at ArcelorMittal Poland S.A.
- Coke plant BO-CARBO
- Coke plant "Walbrzych"
- Coke plant "Czestochowa Nowa"
- Coke plant "Czestochowa"
- Coke plant "Bytom"
- Coke plant "Dabrowa Gornicza"
- Coke plant "Nowa Huta"
- Coke plant "Radlin"

Russia

Baltic Sea

Czech Republic

Slovakia
The production of coal tar (2007 – 2012)
## Properties of coal tar from Polish coke producers

<table>
<thead>
<tr>
<th></th>
<th>Przyjaźń</th>
<th>Victoria</th>
<th>Częstochowa</th>
<th>Bytom</th>
<th>Jadwiga</th>
<th>Radlin</th>
<th>Debieńsko</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content [%]</td>
<td>3</td>
<td>1,3</td>
<td>3,9</td>
<td>2,4</td>
<td>1,4</td>
<td>2,4</td>
<td>2,8</td>
<td>2,6</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>1,192</td>
<td>1,159</td>
<td>1,196</td>
<td>1,168</td>
<td>1,174</td>
<td>1,183</td>
<td>1,172</td>
<td>1,18</td>
</tr>
<tr>
<td>Toluene insoluble matter [%]</td>
<td>10,12</td>
<td>2,80</td>
<td>8,08</td>
<td>6,34</td>
<td>5,69</td>
<td>8,26</td>
<td>4,69</td>
<td>6,71</td>
</tr>
<tr>
<td>Quinoline insoluble matter [%]</td>
<td>5,92</td>
<td>1,37</td>
<td>1,70</td>
<td>3,56</td>
<td>2,68</td>
<td>4,59</td>
<td>2,08</td>
<td>3,13</td>
</tr>
<tr>
<td>Coking value [%]</td>
<td>22,36</td>
<td>14,74</td>
<td>21,24</td>
<td>18,69</td>
<td>18,78</td>
<td>20,80</td>
<td>18,02</td>
<td>19,25</td>
</tr>
<tr>
<td>(ac. PN 88/C-97071)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coking value [%]</td>
<td>28,91</td>
<td>20,30</td>
<td>27,76</td>
<td>24,35</td>
<td>24,73</td>
<td>26,66</td>
<td>23,83</td>
<td>25,28</td>
</tr>
<tr>
<td>(ac. PN 03/C-97093)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash content [%]</td>
<td>0,05</td>
<td>0,03</td>
<td>0,04</td>
<td>0,05</td>
<td>0,03</td>
<td>0,04</td>
<td>0,04</td>
<td>0,04</td>
</tr>
<tr>
<td>Distillation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>begin of boiling</td>
<td>85</td>
<td>114</td>
<td>98</td>
<td>124</td>
<td>106</td>
<td>92</td>
<td>103</td>
<td>102,8</td>
</tr>
<tr>
<td>to 270°C [%]</td>
<td>15,3</td>
<td>15,8</td>
<td>21,3</td>
<td>17,4</td>
<td>17,7</td>
<td>17,4</td>
<td>20,1</td>
<td>17,9</td>
</tr>
<tr>
<td>270-330°C [%]</td>
<td>8,8</td>
<td>11,4</td>
<td>7,0</td>
<td>8,6</td>
<td>10,1</td>
<td>7,5</td>
<td>9,1</td>
<td>8,9</td>
</tr>
<tr>
<td>330-360°C [%]</td>
<td>7,7</td>
<td>9,4</td>
<td>7,2</td>
<td>7,9</td>
<td>7,7</td>
<td>7,4</td>
<td>7,8</td>
<td>7,9</td>
</tr>
<tr>
<td>Residue [%]</td>
<td>67,6</td>
<td>62,1</td>
<td>63,1</td>
<td>65,7</td>
<td>63,3</td>
<td>66,3</td>
<td>62,2</td>
<td>64,3</td>
</tr>
<tr>
<td>lose [%]</td>
<td>0,6</td>
<td>1,3</td>
<td>1,4</td>
<td>0,4</td>
<td>1,1</td>
<td>1,4</td>
<td>0,8</td>
<td>1,0</td>
</tr>
</tbody>
</table>
Distribution of QI content in coal tar, Shewhart charts
Changes of the parameter of coal tar obtained from the same Coke Plant in two series of analysis
Changes of the content QI and TI in coal tar pitches obtained from light and heavy coal tars vs softening point

![Graph showing changes of QI and TI content vs softening point]
Experimental dependence of coal tar pitch softening point vs amount of oil products received during vacuum distillation of coal tar

Range of pressure 10 – 50 kPa

[Graph showing the experimental dependence of coal tar pitch softening point vs amount of oil products received during vacuum distillation of coal tar. The graph includes data points labeled Test 1 to Test 5.]
Properties of coal tar pitches obtained from coal tar in the same industrial line

<table>
<thead>
<tr>
<th>Property</th>
<th>Coal tar</th>
<th>Coal tar pitch, atmospheric distillation</th>
<th>Coal tar pitch, vacuum distillation</th>
<th>Granulated coal tar pitch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening point ac Mettler [°C]</td>
<td>-</td>
<td>45,2</td>
<td>89,7</td>
<td>113,9</td>
</tr>
<tr>
<td>Coking value [%] ac PN 88/C-97071</td>
<td>20,98</td>
<td>31,56</td>
<td>41,20</td>
<td>46,46</td>
</tr>
<tr>
<td>Coking value [%] ac PN 03/C-97093</td>
<td>28,49</td>
<td>40,72</td>
<td>50,22</td>
<td>56,08</td>
</tr>
<tr>
<td>QI content [%]</td>
<td>3,70</td>
<td>5,34</td>
<td>9,00</td>
<td>11,46</td>
</tr>
<tr>
<td>TI content [%]</td>
<td>8,05</td>
<td>18,11</td>
<td>29,66</td>
<td>33,86</td>
</tr>
<tr>
<td>Ash content [%]</td>
<td>0,05</td>
<td>0,10</td>
<td>0,12</td>
<td>0,13</td>
</tr>
</tbody>
</table>
Research capability of Institute

Institute for Chemical Processing of Coal have long – term experience in studies of coal tar and coal tar pitches.

Researches are carried out in:

- Laboratory of Processing Gases and Liquid Derivatives, including accredited by PCA laboratory of analyses coal tar, oils and pitches
- Laboratory of Pyrolysis, including research stand for thermogravimetric studies connected with GC – MS and FT – IR

Current analyses of coal tars from Polish coking plants are made in ICHPW.
Surface tension of coal tar pitches
The method of a lying drop

The big drop \( d/2h < 1.66, 2.18 \)

Porters equation

\[ \sigma = g \Delta \rho \alpha^2 \quad \Delta \rho = \rho_{\text{pitch}} - \rho_{\text{gas}} = \rho_{\text{pitch}}, \quad \alpha = (\alpha_1 + \alpha_2)/2 \]

\[ \frac{\alpha^2}{x^2} = \left( \frac{h}{x} \right)^2 - 0.66 \left( \frac{h}{x} \right)^3 \left[ 1 - 4.05 \left( \frac{h}{x} \right)^2 \right] \]
The stages of surface tension measurement hard coal tar pitch
The stages of wettability measurement

**Vacuum coal tar pitch**

- 112°C, α = 85°
- 126°C, α = 35°
- 138°C, α = 26°

**Granulated coal tar pitch**

- 120°C, α = 89°
- 132°C, α = 49°
- 142°C, α = 39°
Wetting of different electrode surface by impregnation pitch
Relation between contact angle of coal tar binder as a function of temperature, determined on the different surfaces

- CTP coke
- raw anthracite
- calcinated anthracite
- mixing coke
- PCcoke NP. 10 -4
- PCcoke NP. 4-1
- graphite

Contact angle [°] vs. temperature, C
Exampled TG curves of coal tar pitches

TG and DTG profiles of the coal tar pitches:
(A) – atmospheric,
(B) – granulated,
(C) – vacuum.
Three heating rates:
green – 5K/min,
blue – 10K/min,
red – 24K/min.
Summary and conclusions

⇒ Diversified and good recognized basic properties of coal tar allow you to compose the batch to distillation process for obtaining a coal tar pitches with assumed properties depending on the application.

⇒ An important factor affecting the properties of the produced coal tar pitches is an appropriate choice of technological configuration of distillation process.

⇒ Use of advanced physicochemical studies of thermal properties connected with model calculations give additional possibility of coal tar pitch parameters prediction.

⇒ Unfortunately in Poland are not any installation for coal tar distillation for implementation results of our studies, in the past we had five factories of coal tar processing.
THANK YOU FOR YOUR KIND ATTENTION

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