RESEARCH ON PRESSURE SWING EXTRACTION OF COAL TO RECEIVE LIQUID AND LOW-E COAL FUEL

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PRESENTATION PLAN

1. Introduction
2. Purpose of laboratory investigations
3. Methodology of research
4. Analysis of results
5. Summary
6. Bibliography
Microscopical characterization of carbon materials derived from coal and petroleum and their interaction phenomena in making steel electrodes, anodes and cathode blocks for the Microscopy of Carbon Materials Working Group of the ICCP

International Journal of Coal Geology, 139, (2015), 63-79
Pyrolysis of coal is a high-temperature degasification of coal without air in the coke oven batteries included in an installation for the production of coke [1].

Generally during coal pyrolysis we get a number of the following products:

- coke: 70 - 80%,
- crude coke oven gas: 12 - 18%,
- coal tar: 2.5 - 4.5%,
- post-reaction water: 3 - 5%,
- BTEX: do 1%,
- ammonia (as ammonia or as dinitrogen): do 0.4%,
- elemental sulfur: do 0.2%
It is believed that over 10,000 different compounds make up coal tar but only 400 or so have been identified. The main groups of compounds making up crude coal tar are 48% hydrocarbons, 42% carbon and 10% water. The composition of this mixture also includes Polycyclic Aromatic Hydrocarbons (PAHs) [1].

The most common compounds of the coke tar include: naphthalene (10%), phenanthrene (5%), fluoranthene (3.3%) pyrene (2.1%), acenaphthylene (2%), chrysene (2%), fluorene (2%), anthracene (1.8%), carbazole (1.5%) [2].
Fig. 1 Comprehensive processing of typical coal tar [4-6]
EXTRACTION OF COAL

Solvent extraction has always been one of the most commonly used techniques for studying the composition of coal. However, the extraction of coal can be regarded as a process that delivers a number of valuable products/semi-finished products with potential application in different industries.

The factors that have the greatest impact on the process of extraction of coal are [5,6]:

• type of solvent,
• type of coal,
• temperature, time and pressure of the process.
Oele and co-workers abated that in the study of coal extraction, the following groups of operations should be distinguished [7]:

- non-specific extraction (temperatures blow 100°C),
- specific extraction (temperatures blow 200°C),
- extractive disintegration (temperatures higher up 200°C),
- extractive chemical disintegration (temperatures higher up 300°C).
The aim of the work is to study the process of obtaining liquid coal without coking, but the coking process is treated as a point of reference.

The study aimed to investigate the effect of:

- a) temperature,
- b) pressure.
- c) time
- d) the type of solvent,
- e) type of coal (different coal rank)

the yield and quality of the resulting liquid output.

Coal liquids were also tested for use as a binder for the electrode industry.
EXTRACTION OF COAL

COAL
(particle size < 0.2 mm)

SOLVENT

EXTRACTION OF COAL

FILTRATION

post-extraction
coal

liquid coal +
solvent

DISTILLATION

LIQUID COAL

Fig. 2 A block diagram of the extraction process
Fig. 3 The vision of the possibility of development of post-extraction coal
Selected following starting materials are:

- lignite "Bełchatów"
- coal "Bogdanka"
- lignite "Turow"
- coal "Ziemowit,

Tab. 1 Elemental and technical analysis starting materials

<table>
<thead>
<tr>
<th></th>
<th>Technical analysis ,%</th>
<th>Elemental analysis , %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W^a</td>
<td>A^a</td>
</tr>
<tr>
<td>Lignite Bełchatów</td>
<td>12,30</td>
<td>21,10</td>
</tr>
<tr>
<td>Coal Bogdanka</td>
<td>3,40</td>
<td>6,70</td>
</tr>
<tr>
<td>Lignite Turow</td>
<td>15,00</td>
<td>25,10</td>
</tr>
<tr>
<td>Coal Ziemowit</td>
<td>7,10</td>
<td>14,30</td>
</tr>
</tbody>
</table>
### SOLVENTS

Tab. 2 Characteristics of the solvent used for the extraction process

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molar mass, g mol(^{-1})</th>
<th>(t_{\text{boiling}}, ^\circ\text{C})</th>
<th>(t_{\text{critical}}, ^\circ\text{C})</th>
<th>(P_{\text{critical}}, \text{MPa})</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol*</td>
<td>32,04</td>
<td>64,00-65,00</td>
<td>240,00</td>
<td>78,50</td>
</tr>
<tr>
<td>n-hexane</td>
<td>86,18</td>
<td>67,00-69,00</td>
<td>234,00</td>
<td>29,70</td>
</tr>
<tr>
<td>toluene</td>
<td>92,14</td>
<td>110,00-110,63</td>
<td>318,65</td>
<td>4,11</td>
</tr>
<tr>
<td>THF</td>
<td>72,11</td>
<td>66,00</td>
<td>268,00</td>
<td>5,19</td>
</tr>
<tr>
<td>tetralin</td>
<td>132,20</td>
<td>207,50</td>
<td>446,00</td>
<td>3,51</td>
</tr>
<tr>
<td>decalin</td>
<td>138,25</td>
<td>196,00</td>
<td>430,00</td>
<td>2,74</td>
</tr>
</tbody>
</table>
FIG. 4 EXTRACTION APPARATUS AT ATMOSPHERIC PRESSURE

FIG. 5 COMBINED PRESSURE REACTORS FOR EXTRACTION IN SUPERCritical CONDITION
RESULTS OF LABORATORY INVESTIGATION

Fig. 6 Dependence degree of conversion of coal to liquid in function of time for atmospheric pressure extraction

a) Lignite „Bełchatów”
b) Lignite „Turów”
c) Coal „Bogdanka”
d) Coal „Ziemowit”
Fig. 7 Dependence degree of conversion of coal to liquid in function of time for extraction in supercritical condition
a) Lignite „Bełchatów”
b) Lignite „Turów”
c) Coal „Bogdanka”
d) Coal „Ziemowit”
RESULTS OF LABORATORY INVESTIGATION

Fig. 8 Dependence degree of conversion of coal to liquid in function of temperature for atmospheric pressure extraction

a) Lignite „Bełchatów”  
b) Lignite „Turów”  
c) Coal „Bogdanka”  
d) Coal „Ziemowit”
Fig. 9 Dependence degree of conversion of coal to liquid in function of temperature for extraction in supercritical condition

a) Lignite „Bełchatów”
b) Lignite „Turów”
c) Coal „Bogdanka”
d) Coal „Ziemowit”
KINETIC STUDIES – ARRHENIUS’S APPROACH

\[ \ln \left( \frac{\alpha_\infty}{\alpha_\infty - \alpha} \right) = kt \]

GRAPH: \( \ln k \) vs. \( \frac{1}{T} \)

\[ \ln A = 0.3706E_a + 0.0381 \]
\[ r^2 = 0.9977 \]
Dynamic area

\[ T = a \tau + b \]

\[ \frac{dT}{d\tau} = a \]

\[ \frac{dT}{d\tau} \approx \text{const} \]
The aim of the studies was to obtain liquid coal with similar properties to coal tar. For this purpose, the comparison criterion are used, which is based on:

a) H/C ratio (for coal tar H/C = 0.5 acc. [4]),

b) standard enthalpy of formation.
RESULTS OF LABORATORY INVESTIGATION

Fig. 10 Dependence H/C ratio of liquid coal in function of time for atmospheric pressure extraction

a) Lignite „Bełchatów”
b) Lignite „Turów”
c) Coal „Bogdanka”
d) Coal „Ziemowit”
RESULTS OF LABORATORY INVESTIGATION

Fig. 11 Dependence H/C ratio of liquid coal in function of time for extraction in supercritical condition

a) Lignite „Bełchatów”
b) Lignite „Turów”
c) Coal „Bogdanka”
d) Coal „Ziemowit”
\[ \Delta_f H^0 = \Delta_c H^0 [1 - f(\Theta)]^{kJ/\text{kg}} \] (1)

where:

\( \Delta_f H^0 \) – standard enthalpy of formation, kJ kg\(^{-1}\),
\( \Delta_c H^0 \) – standard enthalpy of combustion, kJ kg\(^{-1}\),
\( f(\Theta) \) – function correcting the enthalpy of combustion reaction.
FUNCTION CORRECTING THE ENTHALPY OF COMBUSTION REACTION

An oxygen content above 0.3%

\[ f(\Theta) = b_1 \ln(\Theta) + b_2 \Theta^{0.75} + b_3 \]  \hspace{1cm} (2)

where:
\[ \Theta \] - oxygen content expressed in mass percentage, %

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>(b_1)</th>
<th>(b_2)</th>
<th>(b_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaue</td>
<td>0.01379</td>
<td>-0.01393</td>
<td>1.02111</td>
</tr>
</tbody>
</table>

An oxygen content above 20.0%

\[ f(\Theta) = 1 + a_1 \Theta + a_2 \Theta^2 + a_3 \Theta^3 + a_4 \Theta^4 \ldots \] \hspace{1cm} (3)

where:
\[ \Theta \] - oxygen content expressed in mass percentage, %

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(a_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaue</td>
<td>(4.852 \times 10^{-3})</td>
<td>(-1.437 \times 10^{-3})</td>
<td>(8.467 \times 10^{-5})</td>
<td>(-1.660 \times 10^{-6})</td>
</tr>
</tbody>
</table>
## Heat of Combustion

<table>
<thead>
<tr>
<th>Dependence</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dulong</td>
<td>$Q_s = 338.3C + 1443 \left( H - \left( \frac{O}{8} \right) \right) + 94.25 \text{ kJ/kg}$</td>
</tr>
<tr>
<td>Strach and Lant</td>
<td>$Q_s = 340.6C + 14324H - 153,2O + 104,7S \text{ kJ/kg}$</td>
</tr>
<tr>
<td>Steuera</td>
<td>$Q_s = 339,1 \left( C - \left( \frac{3}{8} \right) O \right) + 238,6 \left( \frac{3}{8} \right) O + 1444 \left( H - \left( \frac{1}{16} \right) O \right) + 104,7S \text{ kJ/kg}$</td>
</tr>
<tr>
<td>D’Huart</td>
<td>$Q_s = 339,1C + 1433,7H + 93,1S - 127,3O \text{ kJ/kg}$</td>
</tr>
<tr>
<td>Seyler</td>
<td>$Q_s = 519C + 1625H + O^2 - 17870 \text{ kJ/kg}$</td>
</tr>
<tr>
<td>Gumza</td>
<td>$Q_s = 340,3C + 1243,2H + 62,8N + 190,9S - 98,4O \text{ kJ/kg}$</td>
</tr>
<tr>
<td>Boie</td>
<td>$Q_s = 351,7C + 1162,6H + 104,7S - 1110 \text{ kJ/kg}$</td>
</tr>
<tr>
<td>Dulong-Berthelot</td>
<td>$Q_s = 341,4C + 1444,5H - \frac{1000(N + O - 1)}{8} + 93S \text{ kJ/kg}$</td>
</tr>
<tr>
<td>IGT</td>
<td>$Q_s = 341C + 1323H + 68,5 - 119,4(O + N) \text{ kJ/kg}$</td>
</tr>
<tr>
<td>Chinniwal</td>
<td>$Q_s = 349,1C + 1178,3H + 100,5S - 103,4O - 15N \text{ kJ/kg}$</td>
</tr>
<tr>
<td>VDI acc. Ochęduśki</td>
<td>$Q_s = 339C + 1214 \left( H - \left( \frac{O}{8} \right) \right) + 104S + 226H \text{ kJ/kg}$</td>
</tr>
</tbody>
</table>
\[ \Delta c H^0 = -327,633 \times C^{daf} - 1417,892 \times H^{daf} - 92,768 \times S^{daf} \text{ } \text{kJ/kg} \]  \tag{4}

\[ \Delta c H^0 = \frac{-Q_s}{f(\Theta)} \text{ } \text{kJ/kg} \]  \tag{5}

where:

- \(Q_s\) - heat of combustion, kJ kg\(^{-1}\),
- \(f(\Theta)\) - function correcting the enthalpy of combustion reaction
- \(\Delta c H^0\) - standard enthalpy of combustion, kJ kg\(^{-1}\),
- \(C^{daf} , H^{daf} , S^{daf}\) - content the elements expressed in mass percentage, %
Fig. 12 Modeling algorithm standard enthalpy of the reaction pyrolysis of coal
Fig. 13 A comparison of the standard enthalpy of formation sizes for coal tar and coal liquids obtained from “Ziemowit” coal extraction using tetralin a) at atmospheric pressure, b) under supercritical conditions (Legend 1 – coal tar conception I, 2 – coal tar conception II, 3 – coal tar conception III, 4 – coal liquid (extraction time 60 min), 5 - coal liquid (extraction time 120 min), 6 - coal liquid (extraction time 180 min), 7- coal liquid (extraction time 240 min), 8 - coal liquid (extraction time 300 min))
Tab. 3 Criterion and recommendations for binders used in the electrode industry [6]

<table>
<thead>
<tr>
<th>CRITERION</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conradson Carbon Residue</td>
<td>50%</td>
</tr>
<tr>
<td>Ash content (max)</td>
<td>0,3%</td>
</tr>
<tr>
<td>Quinoline-insoluble content (QI)</td>
<td>&lt;7%</td>
</tr>
<tr>
<td>Toulene-insoluble content (TI)</td>
<td>&lt;25%</td>
</tr>
<tr>
<td>Softening point</td>
<td>&gt;80 - 120°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RECOMMENDATIONS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content (below)</td>
<td>1%</td>
</tr>
<tr>
<td>Start boiling temperature (higher up)</td>
<td>270°C</td>
</tr>
</tbody>
</table>
## RESULTS OF LABORATORY INVESTIGATION

### Tab. 5 Additional Studies of Liquid Coal Obtained by Extraction "Ziemowit" at Atmospheric Pressure

<table>
<thead>
<tr>
<th>CRITERION</th>
<th>60, min</th>
<th>120, min</th>
<th>180, min</th>
<th>240, min</th>
<th>300, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conradson Carbon Residue, %</td>
<td>34</td>
<td>34</td>
<td>35</td>
<td>37</td>
<td>41</td>
</tr>
<tr>
<td>Ash content (max), %</td>
<td>0,1</td>
<td>0,3</td>
<td>0,4</td>
<td>0,6</td>
<td>0,9</td>
</tr>
<tr>
<td>Quinoline-insoluble content (QI), %</td>
<td>4,5</td>
<td>7,6</td>
<td>7,6</td>
<td>7,7</td>
<td>7,8</td>
</tr>
<tr>
<td>Toluene-insoluble content (TI), %</td>
<td>15</td>
<td>14,4</td>
<td>14</td>
<td>13,3</td>
<td>13</td>
</tr>
<tr>
<td>Softening point, °C</td>
<td>61</td>
<td>62</td>
<td>76</td>
<td>81</td>
<td>93</td>
</tr>
</tbody>
</table>

### Recommendations

<table>
<thead>
<tr>
<th>CRITERION</th>
<th>60, min</th>
<th>120, min</th>
<th>180, min</th>
<th>240, min</th>
<th>300, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content (below), %</td>
<td>0,74</td>
<td>0,74</td>
<td>0,73</td>
<td>0,72</td>
<td>0,71</td>
</tr>
<tr>
<td>Start boiling temperature (higher up), °C</td>
<td>156</td>
<td>186</td>
<td>194</td>
<td>254</td>
<td>274</td>
</tr>
</tbody>
</table>
## RESULTS OF LABORATORY INVESTIGATION

**TAB. 6 ADDITIONAL STUDIES OF LIQUID COAL OBTAINED BY EXTRACTION "ZIEMOWIT" IN SUPERCRITICAL CONDITIONS**

<table>
<thead>
<tr>
<th>CRITERION</th>
<th>60, min</th>
<th>120, min</th>
<th>180, min</th>
<th>240, min</th>
<th>300, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conradson Carbon Residue, %</td>
<td>44</td>
<td>48</td>
<td>49</td>
<td>50</td>
<td>51</td>
</tr>
<tr>
<td>Ash content (max), %</td>
<td>0,1</td>
<td>0,2</td>
<td>0,2</td>
<td>0,2</td>
<td>0,3</td>
</tr>
<tr>
<td>Quinoline-insoluble content (QI), %</td>
<td>6,7</td>
<td>7,0</td>
<td>7,7</td>
<td>8,0</td>
<td>8,1</td>
</tr>
<tr>
<td>Toulene-insoluble content (TI), %</td>
<td>25,9</td>
<td>26,4</td>
<td>27,3</td>
<td>32,2</td>
<td>32,9</td>
</tr>
<tr>
<td>Softening point, °C</td>
<td>94</td>
<td>102</td>
<td>102</td>
<td>110</td>
<td>119</td>
</tr>
</tbody>
</table>

### RECOMMENDATIONS

| Sulfur content (below), %                       | 0,54    | 0,54     | 0,54     | 0,55     | 0,55     |
| Start boiling temperature (higher up), °C       | 254     | 268      | 284      | 294      | 302      |


## RESULTS OF LABORATORY INVESTIGATION

TAB. 7 Fractional composition of the liquid coal obtained at atmospheric pressure

<table>
<thead>
<tr>
<th>Fractional composition, % (w/w)</th>
<th>Extraction time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>11,3</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>2,7</td>
</tr>
<tr>
<td>$\beta$</td>
<td>11,5</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>74,5</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>100</td>
</tr>
</tbody>
</table>
RESULTS OF LABORATORY INVESTIGATION

TAB. 8 Fractional composition of the liquid coal obtained in supercritical conditions

<table>
<thead>
<tr>
<th>Fractional composition, % (w/w)</th>
<th>Extraction time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180</td>
</tr>
<tr>
<td>α₁</td>
<td>19,2</td>
</tr>
<tr>
<td>α₂</td>
<td>8,1</td>
</tr>
<tr>
<td>β</td>
<td>12,3</td>
</tr>
<tr>
<td>γ</td>
<td>60,4</td>
</tr>
<tr>
<td>Σ</td>
<td>100</td>
</tr>
</tbody>
</table>
POST-EXTRACTION COAL

Fig. 14 Comparison of the sulfur content in the output and post-extraction coal

Fig. 15 Comparison of the nitrogen content in the output and post-extraction coal
Fig. 16 Comparison of the LHV value in the output and post-extraction coal
SUMMARY – PART I

a) The best solvent – TETRALIN (for all coal)

b) The highest degree of conversion – coal „Turów”, extraction in supercritical conditions

c) The analysis of the calculations carried out that derived liquids coal (liquid coal obtained in supercritical conditions while 240 and 300 minutes from coal "Ziemowit using tetralin) have a value comparable to a standard enthalpy of formation as coal tar.

d) Studies performed (ash content, the softening point, the sulfur content, the beginning of the boiling point or QI and TI) shows that the liquid coal obtained in supercritical conditions at the time 240 and 300 minutes from coal "Ziemowit" is characterized by a potential properties desired by electrode industry.
SUMMARY – PART II

- BINDER
- PITCH COKE, PITCH COKE, PETROLEUM COKE, ANTHRACITE
- MIXING
- PETROLEUM PITCH
- FORMING
- BACKING
- GRAPHITIZING
SUMMARY – PART II

BINDER → PITCH → PF

COKE, PITCH COKE, PETROLEUM COKE, ANTHRACITE

MIXING

FORMING

GRAPHITIZING

BACKING
<table>
<thead>
<tr>
<th></th>
<th>CRUDE COAL TAR (% m/m)</th>
<th>LIQUID COAL (CC, tetralin, 5h) (%) m/m</th>
<th>LIQUID COAL (CC, decalin, 5h) (%) m/m</th>
<th>LIQUID COAL (AP, tetralin, 5h) (%) m/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>9,845</td>
<td>0,5322</td>
<td>11,6411</td>
<td>0,044</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0,559</td>
<td>0,0009</td>
<td>0,0022</td>
<td>0,003</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>0,748</td>
<td>0,0045</td>
<td>0,0040</td>
<td>1,551</td>
</tr>
<tr>
<td>Fluorene</td>
<td>1,636</td>
<td>0,0038</td>
<td>0,0023</td>
<td>0,006</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>3,534</td>
<td>0,0026</td>
<td>0,0017</td>
<td>0,008</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1,102</td>
<td>0,0006</td>
<td>0,0006</td>
<td>0,020</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>2,265</td>
<td>0,0006</td>
<td>0,0003</td>
<td>0,011</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1,948</td>
<td>0,0008</td>
<td>0,0004</td>
<td>0,013</td>
</tr>
<tr>
<td>Benz[a]anthracene</td>
<td>1,117</td>
<td>0,0010</td>
<td>0,0004</td>
<td>0,003</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0,708</td>
<td>0,0029</td>
<td>0,0011</td>
<td>0,003</td>
</tr>
<tr>
<td>benzo[b+k]fluoranthene</td>
<td>1,081</td>
<td>0,0044</td>
<td>0,0011</td>
<td>0,012</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>0,206</td>
<td>0,0007</td>
<td>0,0009</td>
<td>0,004</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>0,244</td>
<td>0,0008</td>
<td>0,0004</td>
<td>0,002</td>
</tr>
<tr>
<td>Perylene</td>
<td>0,096</td>
<td>0,0004</td>
<td>0,0002</td>
<td>0,004</td>
</tr>
<tr>
<td>Dibenz(a,h)anthracene + Indeno[1,2,3-cd]pyrene</td>
<td>0,355</td>
<td>0,0001</td>
<td>0,0001</td>
<td>0,001</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>0,398</td>
<td>0,0004</td>
<td>0,0001</td>
<td>0,001</td>
</tr>
<tr>
<td>(\Sigma)PAHs</td>
<td>25,848</td>
<td>0,557</td>
<td>11,657</td>
<td>1,686</td>
</tr>
</tbody>
</table>
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THANK YOU FOR YOUR ATTENTION