INCAR Research on Coal Derivatives

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Instituto Nacional del Carbón, CSIC.
Oviedo, Spain

ITA Annual Conference, Palma de Mallorca, June 2007
- The National Institute of Coal (INCAR)
- INCAR research on pitch
  - Pitch generalities
  - Pitch modification
    - Thermal treatment
    - Mesophase separation
    - Oxidative treatment
  - New tendencies
    - Hybrid pitch
    - Anthracene oil-based pitch
- Concluding remarks
Founded in 1947 to assist the local mining and steel industry

- CSIC area: Chemistry and Chemical Technology
- Headquarters in Oviedo (Asturias)
Researchers under contract 32
Research students 30
Scientists 31
Temporary staff 62
Adminstrative and research support 43
Permanent staff 74
TOTAL 136
Research Topics

Coal Conversion

- the optimisation of the coking process for the metallurgical coke production.
- the upgrading of precursors of carbon materials with the aim of improving the competitiveness of these materials, reducing their environmental impact and developing new coal-derived products.
- the pollution caused by the utilisation of coal (evaluation and reduction).
- the feasibility of the carbonisation process as an alternative way of recycling industrial residues and plastic residues from the consumer sectors.
- the chemistry of ionic liquids and their application to reactions of PAHs and the treatment of pitch precursors for the preparation of carbon materials.
Research Topics

Energy and Environment

Optimisation of energy resources related with the utilisation of coal and the reduction of pollutants.

- optimisation of coal blends for hydrogen generation.
- mechanisms of formation and reduction of NOx.
- design and preparation of adsorbents for the purification of gases and liquids.
- CO₂ capture in energy processes based on high temperature treatment (carbonation/calcination).
- CO₂ capture in combustion and gasification at moderate temperatures, based on the development of low-cost adsorbents with specific functionalities for the preferential adsorption of CO₂.
Chemistry of Materials

- Functionalisation of nanostructured materials.
- Preparation of carbon fibres, polygranular synthetic graphites, special cokes and carbon foams from different coal derivatives.
- Development of C/C composites for extreme conditions (aeronautic and nuclear fusion).
- Carbon materials for the production and storage of energy (batteries and supercapacitors).
- Preparation, characterisation and applications of porous materials.
- Colloidal synthesis of ceramic-ceramic and ceramic-metal nanocomposites for biomedical and microelectronic applications.
Regional, national and European Programmes

- EU (RFCS, VI-FP) 13
- National Programmes 20
- R&D Contracts 17
- Regional Government 5
External Relations

National and Foreign Industries, Universities and Research Centers

Bilateral Actions
Exchange of researchers
R&D Projects
R&D Contracts
INCAR Research on Pitches
INCAR Research Topics on Pitches

• Composition, structure, pyrolysis behaviour of pitches with a view to understand their transformation into a carbon material and material performance.

• Specific carbon precursors with improved properties from commercial pitches for advanced carbon materials.

• Feasibility of new pitches as potential binder and impregnant for industrial purposes (e.g., carbon anodes and graphite electrodes)
COAL-TAR PITCH
1 in 4 molecules has a CH$_2$-CH$_3$ group

PETROLEUM PITCH
1 in 4 molecules contains S atom

AR-NAPHTHALENE-BASED PITCH


Mitsubischi Gas Chemical Company, Inc.
Coal-tar pitch composition

- Dibenzo[a]anthracene
- Anthracene
- Acridine
- Phenanthrene
- Benzo[a]fluorene
- Indeno[1,2,3-cd]pyrene
- Coronene
- Carbazole
- Fluoranthene
- Pyrene
- Benzo[j]fluoranthene
- Perylene
- Chrysene
- Dibenzofuran
- Dibenzothiophene
- Benzo[a]fluorene
- Benzo[j]fluoranthene
- Perylene
- Indeno[1,2,3-cd]pyrene
- Coronene
Coal-tar pitch composition - II

Molecular weight (amu)

Pitch Fraction (%)

Coronene (290)
Pitch carbonization

Pitch → Mesogens → Mesophase → Coke → Graphite

∆T

1000 K → 1500 K → 1700 K → 2000 K
Pitch carbonization. Mesophase

Mesophase (CTP)

Mesophase (PP)

(AR-NP)

50 µm
Pitch carbonization. Coke

Coke (CTP)

Coke (PP)

(AR-NP)

50 µm
Pitch as a Precursor for Advanced Carbon Materials

**ADVANTAGES**

- Highly aromatic (graphitizability)
- Adequate viscosity
- High carbon yield
- Good adhesion (carbon particles)
- Highly available
- Low cost
Industrial Pitch as a Carbon Precursor

- Swelling
- Brittleness
- Porosity
Industrial Pitch as a Carbon Precursor - II

ADVANCED USES
- Carbon fibres
- Carbon composites
Modification of Pitches
Why pitch should be modified? How pitch can be modified?

- To reduce porosity
- To increase carbon yield
- To design a carbon precursor with specific properties

Pitch modification

- THERMAL TREATMENT IN AN INERT ATMOSPHERE
- THERMAL TREATMENT IN THE PRESENCE OF AIR (air-blowing)
Thermal treatment of pitches

- Interrupted carbonization (350-450 °C)
- Inert atmosphere (N₂)
- Distillation
- Polymerization (planar macromolecules)
## Thermal treatment of pitches - II

<table>
<thead>
<tr>
<th>Pitch</th>
<th>Treatment</th>
<th>C/H</th>
<th>SP</th>
<th>Ti</th>
<th>NMPI</th>
<th>CY</th>
<th>M</th>
<th>Ø</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>None</td>
<td>1.68</td>
<td>95</td>
<td>21.3</td>
<td>4.9</td>
<td>49.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>A1</td>
<td>420 °C / 6 h</td>
<td>2.01</td>
<td>178</td>
<td>55.2</td>
<td>36.7</td>
<td>72.8</td>
<td>30.0</td>
<td>10-30</td>
</tr>
<tr>
<td>A2</td>
<td>420 °C / 7 h</td>
<td>2.06</td>
<td>202</td>
<td>60.7</td>
<td>40.5</td>
<td>77.3</td>
<td>39.4</td>
<td>10-40</td>
</tr>
<tr>
<td>A3</td>
<td>420 °C / 8 h</td>
<td>2.08</td>
<td>222</td>
<td>63.8</td>
<td>43.1</td>
<td>78.8</td>
<td>41.6</td>
<td>20-40</td>
</tr>
</tbody>
</table>

- **C/H**, carbon/hydrogen atomic ratio
- **SP**, softening point (Mettler, °C)
- **TI**, toluene-insoluble content (wt.%)
- **NMPI**, N-methyl-2-pyrrolidinone-insoluble content (wt.%)
- **CY**, carbon yield (Alcan, wt.%)
- **M**, mesophase content (vol.%)
- **Ø**, sphere mean diameter (μm)

- Dehydrogenative polymerization
- Increasing in SP
- Increasing in TI and NMPI
- Increasing in CY
- Mesophase formation
- Spheres of larger size
Separation of phases in TT pitches. Motivations

- **PITCH**
- THERMALLY TREATED PITCH (Isotropic phase + Mesophase)
  - ISOTROPIC PHASE
  - MESOPHASE

- **SCIENTIFIC**: To study the partial contribution of each phase to the whole pitch
- **TECNOLÓGICO**: To obtain new precursors for carbon materials, especially mesophase

**MESOPHASE ISOLATION**
- Filtration
- Sedimentation
HOT FILTRATION UNDER PRESSURE

- Phases with different softening point
- Filtrated consisting of 100% isotropic phase
- Filtration residue enriched in mesophase (85-95 vol.%)
- No coalescence of the mesophase
- Phases are not altered

Stainless steel reactor
300-350 °C
0.5 MPa N₂
Filter 5 μm mesh
500 g pitch

COAL-TAR PITCH
Separation of phases in TT pitches. Characteristics

<table>
<thead>
<tr>
<th>Pitch</th>
<th>M</th>
<th>C/H</th>
<th>SP</th>
<th>TI</th>
<th>NMPI</th>
<th>CY</th>
</tr>
</thead>
<tbody>
<tr>
<td>TT430-3</td>
<td>25</td>
<td>1.89</td>
<td>174</td>
<td>53.9</td>
<td>29.8</td>
<td>61.5</td>
</tr>
<tr>
<td>Isotropic Phase</td>
<td>0</td>
<td>1.85</td>
<td>169</td>
<td>45.8</td>
<td>16.3</td>
<td>56.2</td>
</tr>
<tr>
<td>MESOPHASE</td>
<td>80</td>
<td>2.05</td>
<td>-</td>
<td>66.7</td>
<td>53.4</td>
<td>74.9</td>
</tr>
</tbody>
</table>

M, mesophase content (vol.%)
C/H, carbon/hydrogen atomic ratio
SP, softening point (Mettler, °C)
TI, toluene-insoluble content (wt.%)
NMPI, N-methyl-2-pyrrolidinone-insoluble content (wt.%)
CY, carbon yield (900 °C, wt.%)

Mesophase is more polymerized than the isotropic phase
Treated pitch a combination of the two phases
Separation of phases in TT pitches. Applications

**ISOTROPIC PHASE**
- O.T. coke highly orientated
- CARBON FIBRES

**MESOPHASE**
- Homogeneous-size spheres
- POLYGRANULAR GRAPHITES
Mesophase isolation. Sedimentation

HOT SEDIMENTATION

\[ 400-450 \, ^\circ\text{C} \, (\sim 420 \, ^\circ\text{C} \, , \, 1\text{h}) \]

\[ \text{Phases with different density} \]

\[ \text{Bottom phase almost 100 \% mesophase} \]

\[ \text{Phases are not altered} \]
## Mesophase properties and applications

<table>
<thead>
<tr>
<th>Pitch</th>
<th>M</th>
<th>C/H</th>
<th>SP</th>
<th>TI</th>
<th>NMPI</th>
<th>CY</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0</td>
<td>1.52</td>
<td>127</td>
<td>3.6</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>TT-PP</td>
<td>28</td>
<td>1.95</td>
<td>210</td>
<td>52.9</td>
<td>27.0</td>
<td>78.5</td>
</tr>
<tr>
<td>MESOPHASE</td>
<td>96</td>
<td>2.14</td>
<td>317</td>
<td>76.5</td>
<td>61.4</td>
<td>86.1</td>
</tr>
</tbody>
</table>

- **M**: mesophase content (vol.%)
- **C/H**: carbon/hydrogen atomic ratio
- **SP**: softening point (Mettler, °C)
- **TI**: toluene-insoluble content (wt.%)
- **NMPI**: N-methyl-2-pyrrolidinone-insoluble content (wt.%)
- **CY**: carbon yield (900 °C, wt.%)

**MESOPHASE** → **CARBON FIBRES**
Oxidative treatment of Pitches

- Temperatures < 350 °C
- Reaction times 10 h
- In the presence of air (oxygen)
- Distillation
- Planar macromolecules
- Cross-linked olygomers
- No mesophase formation
Oxidative treatment of Pitches - II

<table>
<thead>
<tr>
<th>Pitch</th>
<th>Treatment</th>
<th>O</th>
<th>C/H</th>
<th>SP</th>
<th>TI</th>
<th>NMPI</th>
<th>CY</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>None</td>
<td>1.80</td>
<td>1.64</td>
<td>97</td>
<td>20.0</td>
<td>4.7</td>
<td>34.6</td>
</tr>
<tr>
<td>B1</td>
<td>275 °C / 10 h</td>
<td>1.78</td>
<td>1.72</td>
<td>139</td>
<td>36.6</td>
<td>13.6</td>
<td>48.0</td>
</tr>
<tr>
<td>B2</td>
<td>275 °C / 18 h</td>
<td>1.81</td>
<td>1.83</td>
<td>168</td>
<td>44.6</td>
<td>18.1</td>
<td>57.6</td>
</tr>
<tr>
<td>B3</td>
<td>275 °C / 25 h</td>
<td>1.89</td>
<td>1.86</td>
<td>197</td>
<td>51.8</td>
<td>24.9</td>
<td>61.8</td>
</tr>
<tr>
<td>B4</td>
<td>275 °C / 30 h</td>
<td>1.86</td>
<td>1.87</td>
<td>210</td>
<td>52.0</td>
<td>27.1</td>
<td>62.7</td>
</tr>
</tbody>
</table>

O, oxygen content (wt.%)
C/H, carbon/hydrogen atomic ratio
SP, softening point (Mettler, °C)
TI, toluene-insoluble content (wt.%)
NMPI, N-methyl-2-pyrrolidinone-insoluble content (wt.%)
CY, carbon yield (900 °C, wt.%)

- Dehydrogenative polymerization
- No oxygen uptake
- Increase in softening point
- Increase in insoluble content
- Increase in carbon yield
New Tendencies in Pitches
New tendencies in pitches

POLLUTION AND WORKERS HEALTH
(non-controlled environments)

- Emission of toxic and/or carcinogenic PAHs to the atmosphere and the working space

COAL TAR SUPPLY AND LOCATION

- Reduction in coal tar production in the West Europe countries and coal tar produced far away from coal tar distillers
CTP+PP hybrid pitches

COAL-TAR PITCH
- Inherent binder capacity
- Appropriate viscosity and wetting behaviour

PETROLEUM PITCH
- Lower content in metals
- Lower content in genotoxic PAHs

HYBRID PITCH
CTP+PP hybrid pitches

- CTP-A/PP-B (70:30)
- CTP-A/PP-B (55:45)

AB30

PR =
M =
IQ ↓

1 % min⁻¹

Temperature (°C)

CTP-A
AB30
AB45
PP-B

COKES (900 °C)

Benzo[a]Pyrene (ppm)

CTP-A | AB30 | AB45 | PP-B
---|---|---|---
8,276 | 4,958 | 3,297 | 904

Lab carbon anodes (Söderberg) with similar properties
Anthracene oil-based pitches

Why?

• Anthracene oil is highly aromatic

• Representative coal-tar fraction, in terms of percentage (30%)

• Low value product

• It is a heavy coal-tar distillation fraction susceptible to be transformed into pitch

• Uniform composition

• Possibility to produce a semi-synthetic pitch

•.....
Anthracene oil-based pitches - II

1. Acenaphthene
2. Fluorene
3. Phenanthrene
4. Anthracene
5. Fluoranthene
6. Pyrene

- Anthracene oil mainly consists of 3-5 ring PAH
- Components stable at their boiling point
- Condensation cannot be performed by thermal treatment at atmospheric pressure
Anthracene oil-based pitches - III

- Oxidative Aromatic Condensation
- Distillation 90-110 °C, Mettler SP
- Thermal & Chemical Treatment
- 250-295 °C
## Anthracene oil-based pitches - IV

<table>
<thead>
<tr>
<th>Pitch</th>
<th>SP</th>
<th>QI</th>
<th>β-R</th>
<th>S</th>
<th>CY</th>
<th>B[a]P</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-CTP</td>
<td>110</td>
<td>10.0</td>
<td>18-20</td>
<td>&lt; 0.6</td>
<td>53</td>
<td>10.8</td>
</tr>
<tr>
<td>110-AOP</td>
<td>110-115</td>
<td>0.3-1.0</td>
<td>23-28</td>
<td>&lt; 0.6</td>
<td>45-47</td>
<td>1.7-14.0</td>
</tr>
<tr>
<td>I-CTP</td>
<td>90</td>
<td>1.3</td>
<td>15-16</td>
<td>&lt; 0.6</td>
<td>41</td>
<td>12.8</td>
</tr>
<tr>
<td>90-AOP</td>
<td>90</td>
<td>0.3-0.5</td>
<td>20-23</td>
<td>&lt; 0.6</td>
<td>39-41</td>
<td>3.4-14.0</td>
</tr>
</tbody>
</table>

SP, Mettler softening point (°C)
QI, quinoline insolubles (wt.%)
β-R, beta resin content (wt.%)
S, sulphur content (wt.%)
CY, Sers carbon yield (wt.%)
B[a]P, Benzo[a] pyrene content (mg/g)

<table>
<thead>
<tr>
<th></th>
<th>CTP</th>
<th>AOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetting (°C)</td>
<td>135</td>
<td>135-137</td>
</tr>
<tr>
<td>Filtration rate (g)</td>
<td>18 (80 min)</td>
<td>60 (40-50 min)</td>
</tr>
</tbody>
</table>
Anthracene oil-based pitches - V

Severity of the oxidative treatment
Anthracene oil-based pitches - VI

- Uniformity in pitch composition
- High fluidity
- Highly aromatic composition
- Semi-synthetic pitches
- Absence of solid particles & metals
- High flexibility to produce carbons with different O.T.

**ANTHRACENE OIL BASED PITCHES**

**CARBON ANODES**
**CARBON FIBRES**
**SYNTHETIC GRAPHITES**
**CARBON PREFORMS** (Impregnation)
• The main application of coal-tar pitch is as binder and impregnating agent in industrial processes (aluminium and graphite technology).

• Coal-tar pitches can be used as advanced carbon precursors.

• Recent development in pitch production allows pitches from heavy tar distilled fractions (i.e., anthracene oil) to be obtained. AOPs represent a new generation of pitches with specific properties, and consequently, other potential applications which have still not been studied.
Regional Government

- Development of carbon-based supercapacitors for high power electronic applications (2005-2007)
R&D Projects

National Programmes

• Preparation of new binders from petroleum residues for their use in the fabrication of electrodes (1999-2001)
• Preparation of carbon fibres and synthetic graphites from coal-tar pitches (2000-2001)
• New carbon anodes for ion-lithium batteries (2001-2004)
• Development of new petroleum pitches for magnesia-carbon composites (2003-2007)
• Development of nanoporous carbon materials for carbon storage (2004-2007)
• Reduction of carcinogenic emissions in the production of carbon anodes by means of petroleum pitches (2005-2007)
• Carbon materials for lithium ion batteries anodes (2007-2009)
European Programmes

• New materials for extreme environments (2004-2008)