Fuel bricks from lignin and coal fines

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Application: Metal casting

A cupola is a vertical furnace used to melt cast iron; coke is the fuel source.
Coke

When many bituminous coals are heated, they soften, swell and re-solidify into a porous solid
Can lignin-bound anthracite fines become coke substitutes?

Coke properties

The cupola furnace

Lignin-bound anthracite fines
Motivation

- Coking is an energy intensive and highly polluting process, but is necessary to achieve desired morphology of coke.

- Lignin, anthracite fines and collagen are all by-products of existing industries, should be inexpensive.

- There is no other current use for anthracite fines, vast stocks exist.

- Heterogeneity of the lignin is well-tolerated.

- Coking is not needed (saves 20% of material, plus reduced emissions).
Anthracite doesn’t “coke” (expand and fuse), so it isn’t cokable

- High fixed carbon content
- Low volatile matter
- Clean combustion
- High heating values
- Low sulfur and nitrogen
- Hard and brittle
Darker colors represent areas known to contain coal beds that are of commercial value at the present time or that may be of value to the future. In general the minimum thicknesses included are 14 inches for anthracite and bituminous coal, and 30 inches for subbituminous coal and lignite.

Lighter colors represent areas of doubtful value for coal. These may be divided into three classes- (1) areas containing thin or irregular beds, which generally have little or no value, but which locally may be thick enough to mine; (2) areas in which the coal is poor in quality; and (3) areas where information on the thickness and quality of coal beds is meager or lacking.

Source: U.S. Energy Information Administration.
Anthracite processing regions
Anthracite fines were mixed with lignin, collagen, and silicon, then pressed into a briquette.

1 Kg briquettes: 89% anthracite fines, ~5% lignin, 6% other additives.
Pilot test: 8 Tons of bricks were made, tested at 2 foundries

Anthracite fines are held together by collagen, lignin, and SiC.

- Collagen is a binding agent at room temperature.
- Lignin is effective at the medium temperature regime.
- SiC is effective at the high temperature regime.
Lignin thermochemical evolution has been studied ($^{13}$C SS NMR), also Raman (not shown).
Briquette strength has been studied

Lab scale briquettes were pyrolyzed to simulate heat exposure in the cupola.
Reflected light analysis-specimen preparation
Reflected light image of the polished surface of a briquette pyrolyzed at 800°C for 2 h

Figure 2. Reflected light images of polished surfaces of pyrolyzed lignin-bound anthracite briquettes. a) indicates anthracite grains, b) indicates silicon grains, and the arrows point at lignin/collagen amorphous phase
Reflected light images of polished surfaces

1400°C

1600°C
SEM of lignin-bound anthracite fines after 2h pyrolysis

1400°C

1600°C
SEM suggests a difference in the crystal structure from 1400 to 1600°C
XRD analysis of a decarbonized sample that was treated at 1600°C for 2h

- **1600°C**
  - β-SiC
  - Si

- **1400°C**

- **800°C**

- Anthracite ash
Semi-quantitative analysis from XRD data of decarbonized briquettes

<table>
<thead>
<tr>
<th>Mineral/Phase</th>
<th>Raw</th>
<th>800°C</th>
<th>1400°C</th>
<th>1600°C</th>
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<tr>
<td>3C-SiC</td>
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<td>11.1</td>
<td>62.2</td>
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<td>2H-SiC</td>
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<td>5.5</td>
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<td>4H-SiC</td>
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<td>Si</td>
<td>35.9</td>
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<td>16.5</td>
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TEM of a sample treated at 1400°C for 2h, the sample was decarbonized for analysis
TEM of a sample treated at 1600°C for 2h, the sample was decarbonized for analysis.
In conclusion, lignin, collagen and silicon form a binder phase that holds anthracite fine grains.

Reflectance analysis of pyrolyzed briquettes revealed the existence of a binder phase.

Volatilization of lignin and collagen provides strength, leaves round pores of thin walls formed by pressurized and confined gases within the matrix.

Silicon compounds behave as filler phase occupying the interstitial spaces of anthracite grains, at high temperatures form bridges, crystals, nanowires.
Acknowledgements

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Other components added to the cupola furnace

- Si, SiC, FeC, FeSi, FeMn
Elemental analysis of pyrolyzed lignin

<table>
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<th>H</th>
<th>N</th>
<th>S</th>
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<td>Lignin 1400°C</td>
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<td>0.06</td>
<td>0.11</td>
<td>0.89</td>
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