

Introduction

Isotropic cokes are of special interest for the manufacture of isotropic carbon and graphite shapes used in nuclear reactors. At the Carbon Conference at Baden-Baden 1976 it was shown that isotropic cokes can be obtained from pitch precursors to which α -resins (QI) have been added. These cokes cover a wide range of CTE (1). This method requires the separation of both the primary and the secondary α -resins from selected pitches. It is also known that materials like natural bitumina and thermal-setting resins are suited for the manufacture of isotropic cokes. The presupposition for the formation of isotropic coke from pitch is a high reactivity resulting in a three-dimensional crosslinking during the carbonisation. An interesting material with the pre-supposed properties and which is available on the market is the tar formed in the coal pressure vaporisation process.

Experimental

The experiments were performed with tars formed in the coal pressure vaporisation process (CPV). To reduce the content of insoluble matter especially minerals the tars were filtered. The softening point of the tar was increased by distillation. The properties of the resulting pitch are listed in Table 1.

The tars were additionally examined by gas and high pressure liquid chromatography and NMR-spectroscopy. The gas chromatography was performed in the well known technique with a column filled with siliconrubber on Chromosorb. The high pressure liquid chromatography (gel permeation technique) was performed with a column filled with Styragel of 3000 Å, 1000 Å, 500 Å and 100 Å exclusion pore size, a pressure of 51 bar and quinoline as elution liquid. A UV-spectrometer at 370 nm was used as detector. The special technique of gel permeation chromatography for tars and pitches is described in detail in (2). The NMR-spectroscopy was used to characterize the molecular composition of the tars especially to measure the content of the aromatic and aliphatic bonded hydrogen.

The CPV-pitch has been carbonized in laboratory using a heating rate of 25°C/h and in a baking furnace using a heating rate of about 2,5°C/h in the temperature range of between 350 - 450°C. The final temperatures varied between 950 and 1000°C. The resulting cokes were examined by measuring the coefficient of thermal expansion of the coke grains (calcined at 1300°C) as described elsewhere (3).

For detailed information on the isotropic behaviour the relation of the three linear coefficients of thermal expansion of coke cubes were used.

Results

The gas chromatographic examination of the pyridine soluble constituents of the CPV-pitch shows that this matter has only a small content of aromatic compounds having a low molecular weight, like naphthalene or anthracene. The broad underground peak is an evidence of the asphaltenic character of the matter similar to petro-bitumina. The gel permeation chromatography demonstrates that the average molecular weight of the soluble matter is much higher for the CPV-pitch than for a coaltar pitch with a comparable softening point. The good solubility of about 93 % of the CPV-pitch in toluene is caused by its different molecular structure. These differences can be explained by the results of the NMR-spectroscopy proving a larger content of reactive aliphatic and naphthenic molecular groups in the CVP. These reactive groups explain the tendency of this tars to form preferably isotropic coke structures during the carbonisation process.

The coke data (given in Table 2) show that a slow carbonisation rate results in more anisotropic coke structures. By decreasing the heating rate (25°C/h to 2,5°C/h) in the critical temperature range of the coke formation between 350 and 450°C the CTE (volume) is decreased from $13,5$ and $11,3 \cdot 10^{-6}/K$ to $7,3$ and $7,6 \cdot 10^{-6}/K$ respectively and the anisotropy ratio is increased from 1,21 and 1,28 to 1,64 and 1,39 respectively. Obviously a low heating rate enables a better orientation of the pitch constituents during the carbonisation process. Furthermore it can be shown that a low heating rate causes a higher scattering of the measured CTE values.

References

- 1) H. Tillmanns, H. Pauls and G. Pietzka,
Carbon Conf. 1976, p. 374, Baden-Baden
- 2) H. Tillmanns, W. Ulsamer and G. Pietzka,
Carbon Conf. 1976, p. 557, Baden-Baden
- 3) G. Pietzka, G. Wilhelmi and H. Pauls,
Carbon Conf. 1972, p. 362, Baden-Baden

Table 1: Properties of filtered CPV-pitch

	sample 1	sample 2
Softening point (KS) °C	82	104
Coke yield Din 51720 %	18,7	25,6
Coke yield baking furnace %	64,7	63,3
Quinoline insoluble %	0,1	0,1
Toluene insoluble %	6,8	7,2
Methanol insoluble %	75,6	68,9

Table 2: Coke from CVP

	sample 1	sample 2
Laboratory (25°C/h; 350-450°C)		
CTE (volume) · 10 ⁻⁶ /K	13,5	11,3
Anisotropy ratio	1,21	1,28
Baking furnace (2,5 °C/h; 350-450°C)		
CTE (volume) · 10 ⁻⁶ /K	7,3	7,6
Anisotropy ratio	1,64	1,39