PRODUCTION OF CARBON FIBRES FROM CHAR TARS

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Introduction

During the pressure gasification of coals, char tars with high contents of solids are obtained in the temperature range of about 500 to 600° C which, after separation of the constituents insoluble in chinoline, are suitable as base products for the making of carbon fibres. In the following, these tars are called "KDV-tars".

In the same way, tars obtained during the charring of hard coals, e.g. according to the Lurgi-Ruhrgas process, in the temperature range from 500 to 600° C, so-called LR-tars, can be used. The cleaning of such tars is done, without adding any solvents, in a pressure filter at temperatures from 150 to 250° C and filtration pressures from 2 to 6 bar. As filter tissue, metal tissues with a mesh size of about 60 µm are used[1].

Due to the high solid contents in the tars, it is necessary to add 2 to 3 % filtering aids on the basis of diatomaceus earth in order to obtain a filter cake as permeable as possible even with larger cake thicknesses.

Despite of the low particle size (1 to 80 µm) of the solids to be separated, the solid contents could be reduced, by pressure filtration, from about 15 to 20 % in the base tar to < 0.1 % in the final product. In order to increase the softening point to about 130 to 150° C, the purified tars were either subsequently treated by distilling or blasted by air.

Similarly, the purification of the tars was tested in a centrifuge[2] after adding a suitable solvent. Due to the high solid contents in the tar, however, higher degrees of purity were obtained by the pressure filtration.

Spinning Process

In a plant where the fibres are spun above the smelting point, endless fibres with a diameter of 5 to 20 µm were produced at a spinning temperature of about 230° C. In order to avoid a sticking together of the individual fibres during the thermal secondary treatment, the fibres were dusted with an activated carbon impregnated by H_2SO_4. In order to shorten the oxidative secondary treatment with air, an additional short treatment of the fibres (from 1 to 5 minutes) in bromine proved well. The fibres were pushed in a spinning machine by piston pressure through a perforated plate with apertures of 0.3 mm Ø and stretched, via a smoothing mechanism, to the desired Ø between 5 and 20 µm. The fibres were then wound up crosswise on coils and could be wound off the coil continuously during the thermal secondary treatment[3].

Thermal Secondary Treatment

The secondary treatment was carried out in two stages, viz. by oxidation of the fibres in air up to about 400° C in a tubular oven and the subsequent carbonization of the primarily treated carbons under inert gas (N_2). As far as possible, the oxidation time during the various tests was fixed to 60 minutes and the subsequent carbonization to 55 minutes in order to obtain better comparison values with previously measured carbons made from high-temperature tar pitch. The shortest possible oxidation time was taken for samples which could not be oxidized within 60 minutes without sticking together. The activated carbon prepared with oxidizing agents prevents a sticking together of the individual fibres during oxidation. Beyond that, H_2SO_4 is purposively liberated during higher temperatures and accelerates the oxidation of the pitch fibres. With temperatures above 300° C, an increased outlet of low-molecular pitch constituents from the surface of the fibres can be observed, and these very sticky constituents are absorbed by the activated carbon. However, the activated carbon sticks only loosely to the surface of the fibres and does not enter into a connection with the pitch fibres. After the carbonization stage, the activated carbon can be recovered and can be used again after a corresponding impregnation with H_2SO_4.

Results

Very thin fibres with diameters up to 5 µm can be made from LR- and KDV-tar pitches by spinning above the smelting point. Similarly to fibres made from high-temperature tar pitch, the tensile strength increases with smaller diameters of the fibres.

The attainable tensile strengths are plotted in the Figs. 1 and 2 as a function of the diameter of the fibres. For the sake of comparison, the strength curves for high-temperature tar pitches are shown, too[4].

It can be seen from these curves that char pitches are suitable as a base product for making fibres of a high tensile strength. Char tar

pitches blasted by air have a higher tensile strength than pitches secondarily treated by destilling.

Mixtures of high-temperature tar pitch and char tar pitch are not suitable for making fibres of a high tensile strength.

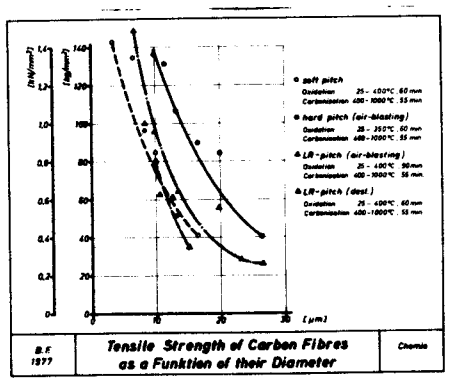

Fig. 1

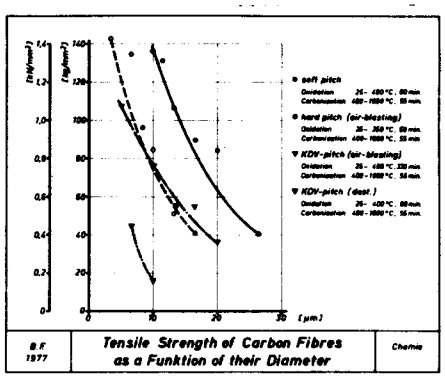

Fig. 2

Summary

With the gasification and charring of coal, char tars are obtained in the temperature range from about 500 to 600° C which, after the separation of constituents insoluble in chinoline and a further secondary treatment, are suitable for the production of carbon fibres by distilling or blasted with air. Char tar pitches with a softening point of about 130 to 150° C can be spun, above the smelting point, at a temperature of 230° C to raw fibres with a diameter of 5 to 20 µm and are then secondarily treated by oxidation in air up to 400° C and carbonization in a nitrogen atmosphere. The tensile strengths then reached depend on the primary treatment of the char tars: they are, for air-blasted char tars, in the range of the tensile strengths of fibres made, according to the same process, from high-temperature tar pitches.

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