EVALUATION OF HOT CENTRIFUGATION PARAMETERS FOR QUANTITATIVE DETERMINATION OF MESOPHASE CONTENT IN PITCH

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Introduction

Mesophase content is an important parameter in the production of pitch-based carbon materials, as it determines their mechanical, thermal and electrical properties. [1]

ASTM D - 4616 is a standard method to determine mesophase content in pitch, but it is only applicable to pitches with mesophase content below 20%[2]. In recent years, other methods for determining higher mesophase contents were developed. Separation of the denser mesophase by hot centrifugation has been used successfully by Vieira[3] and others, but its accurate quantification still presents challenges. Care also must be taken to avoid modification of mesophase content in the pitch sample by extended exposure to high temperatures.[4]

The objective of the present work is to analyze the effects of time and temperature of hot centrifugation on the accuracy of mesophase content, and propose an improvement in technique proposed by Vieira, changing the manually separation of phases for a more scalable process.

Materials and Methods

Four self-made petroleum pitches with increasing mesophase content were used for determination of isotropic and mesophase densities. Around 20 g of each pitch were centrifugated for 60 min, at 60 rps and 330 °C, separated into isotropic and mesophase portions, milled and analyzed in a helium pycnometer according to ASTM D-4892.[5] Softening point (SP) was determined through rheology analisys.[6]

Table 1: Isotropic and anisotropic pitch densities.

Pitch	Softening Point (°C)	Isotropic Density (g/cm^3)	Anisotropic Density (g/cm^3)
A	169	1,2845	1,3460
B	224	1,2972	1,3490
C	259	1,3060	1,3417
D	298	1,2970	1,3451
	Average	1,2962	1,3454

The selected pitches were centrifugated according to Vieira's method, with variable conditions of time (30 min, 45 min, 60 min and 75 min) and temperature (Softening Point + 10°C, 20°C, 50°C, 75 °C, and 100 °C).

Based on the values obtained on table 1, a sulfuric acid solution of intermediate density was prepared (40 mL of sulfuric acid and 100 mL of distillated water). Sulfuric acid was chosen due to its density of1,84 g/cm^3, inorganic and polar nature, minimizing interactions with pitch molecules.

For the proposed method, samples were manually milled, inserted on sulfuric solution for 1h, filtrated, washed with distilled water and dried until the weight oscillation became residual.

Results and Discussion

Analysis of the effect of centrifugation temperature on measured mesophase content suggest the existence of three regions. At lower temperatures, viscosity is too high for adequate phase separation and mesophase remains entrapped in the isotropic phase, for pitches of low SP, or vice-versa, for

pitches of high SP. Proper mesophase separation occurs at intermediate temperatures, different for each pitch. At higher temperatures, mesophase content may be modified by further mesophase formation or volatile loss. Rheological properties of the samples studied in this work suggest that adequate temperatures for mesophase separation are in the range corresponding to a viscosity of 10-20 Pa.s. At these conditions, 30-45 minutes were sufficient for phase separation (Figure 2.b), and lower centrifugation times will be further evaluated, as shorter analysis times reduce the risk of sample modification.

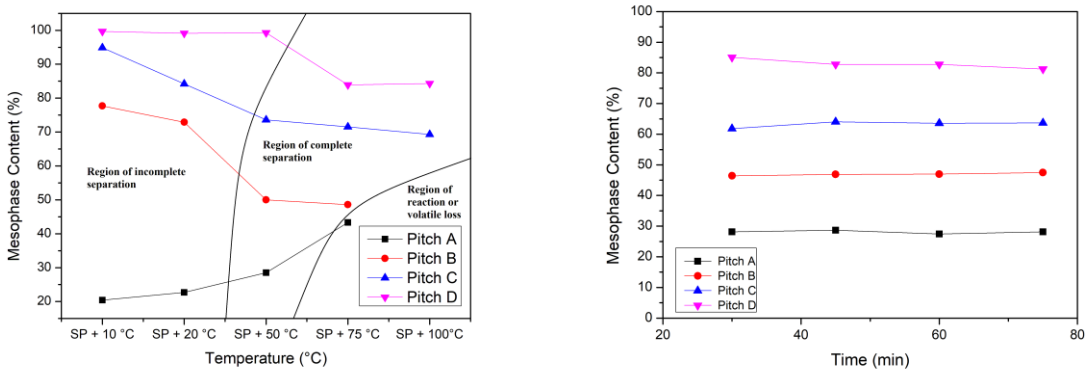

Figure 1. a) Temperature analysis and b) Time analysis.

Table 2: Viscosity at separating temperature.

Pitch	Viscosity (Pa.s)
A at 220 °C	15.26
B at 299 °C	21.40
C at 330 °C	14.20
D at 370 °C	08.50

Table 3: Comparison between methods.

Pitch	Original Method		Proposed Method	
	Mesophase (%)	Standard Deviation	Mesophase (%)	Standard Deviation
A	28	1,2	34	3,5
B	43	1,4	45	10,2
C	71	0,4	71	3,6
D	84	0,1	79	4,8

Comparison between the manual method for separation and quantification, proposed by Vieira, and a new separation method based on flotation process showed similar values for mesophase content, but inadequate repeatability. Longer flotation times and use of a lab centrifuge for phase separation in the acid solution will be evaluated to improve method repeatability.

Conclusions

Mesophase quantification by hot centrifugation can be optimized, both in time and temperature, according to pitch softening point. A new method for quantification of phases in the centrifuged sample showed potential, but needs to be further optimized to improve repeatability.

References

1. Inagaki, M., Kang, F. Materials Science and Engineering of Carbon: Fundamentals. 2014. Chapter 1.
2. ASTM D–4616. Standard Test Method for Microscopical Analysis by Reflected Light and Determination of Mesophase in a Pitch.
3. Vieira, R. F. Dutra, C. H. M. C., de Castro, L. D. Determining the anisotropic content in a petroleum pitch – Comparison of centrifugation and optical microscopy techniques. Fuel, vol 90, pp 908-911. 2011.
4. Izumi et al. Process for producing mesophase pitch. 1981. Japan.
5. ASTM D-4892. Standard Test Method for Density of Solid Pitch.
6. Braga, C. P., et al. Influence of heat pressure treatment on rheological behavior of petroleum pitches. Fuel, Vol 88, N 5, p 853-860. 2009.