THE STUDY OF QI EXTRACTION FROM COAL TAR PITCH USING COAL-TAR-DERIVED OILS AS SOLVENT IN A CENTRIFUGATION PROCESS

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Introduction

Quinoline Insoluble (QI) fraction is a very complex important component of pitches, which remains as one of the subjects intensively investigated even in this decade. While the optimization of mechanical properties of synthetic graphite can be ascribed to the adequate choice of binder pitch with specific range of QI contents, the development of special form of carbon, such as carbon fibers, depends on the pitches from which the natural QI has been completely removed [1-2].

Many physical and/or chemical methods can be applied to the pitch QI extraction process. The dilution of pitch by coal-tar-derived organic oils followed by physical separation has been noticed to be efficient [3-5].

The aim of the present work is to recognize the basic chemical components of several organic oils produced at a metallurgical coke production plant, as well as their efficiency as QI extraction agent.

Experimental

A soft pitch, commercial product by USIMINAS, was selected for this study . Main characteristics are: Softening Point (SP) = 40.0°C, Quinoline Insoluble (QI) = 3.5%; Toluene Insoluble (TI) = 12.1%, Volatile Matter (VM) = 64,7%, Ash = 0.1 %, Fixed Carbon (FC) = 35.2 %, C = 92,8%, H = 4,9%, N = 1,5 %, S = 0,5%, O = 0,2 %, H/C = 0,63.

To produce a low viscosity liquid from soft pitch using a centrifugation process, industrial grade quinoline and five different coal-tar-derived oils were used as solvents. Those coal-tar-derived oils are produced at USIMINAS coking facilities. They are denominated as phenolic oil 1 (PO1), phenolic oil 2 (PO2), naphthalene oil (NO), intermediate oil (IO), washing oil (WO) and heavy oil (HO). A schematic flow chart of the USIMINAS distillation process where these coal tar oils are produced is shown in figure 1.

The process of QI extraction used the pitch diluted in solvents (1:3 v/v proportion). It was performed in three steps : 1) digestion of the soft pitches in each solvent at 90 to 95°C during 20 min under constant stirring; 2) semi-continuous laboratory scale centrifugation at 4000 rpm; 3) distillation at 300°C to remove the remaining solvent. The last step of the process was also applied to the green soft pitch, without dilution, to be used as a standard pattern for heat treatment conditions.

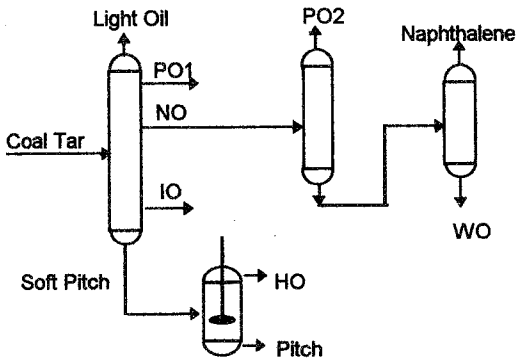

Figure 1. Schematic flow chart of USIMINAS coal tar distillation process.

The solvent oils were characterized by gas chromatography coupled with mass spectrometry (GC-MS). The pre treated soft pitches by solvent dilution and by distillation treatment were analyzed to observed QI, TI contents and softening point temperatures.

Results and Discussion

The GC-MS analysis of all oils confirmed and identified 44 different hydrocarbon compounds. The lighter oils (PO1 and PO2) are constituted, mainly, by a mixture of monocyclic aromatic compounds having methyl, ethyl and phenol radicals, although a small number of dicyclic compounds led by indene were also identified.

The NO and WO oils may be classified as intermediate weight oils. They are all, essentially constituted by dicyclic aromatic compounds, headed by

naphthalene and its derivative products. It was also noted the presence of heteroatomic compounds, namely quinoline and dibenzofurane, in WO.

The heavier oils (IO and HO) produced in this distillation process are rich in polycyclic hydrocarbon molecules. They are distinguished by the presence of phenantrene as the main component.

Results from all oils analyzed revealed that naphthalene is present in the individually distilled coal tar oils, as showed in figure 2.

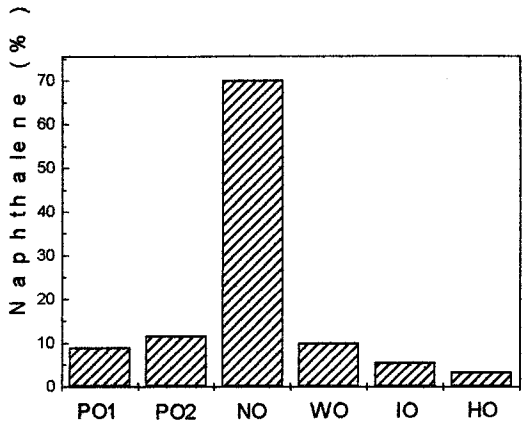

Figure 2. Naphthalene content in coal-tar-derived oils from USIMINAS coking plant.

The results of analysis of distilled soft pitches and solvent treated pitches after the centrifuge separation process are presented in the Table I.

Table I. Softening points, Quinoline and Toluene Insolubles fractions of the pre-treated soft pitches.

Solvent	SP (°C)	QI (%)	TI (%)
soft pitch	46.0	4.6	13.8
soft pith/Q	47.0	0.7	5.6
soft pitch/PO1	64.1	0.8	15.7
soft pitch/PO2	60.6	1.4	15.2
soft pitch/NO	49.7	0.3	10.7
soft pitch/WO	45.3	0.2	9.7
soft pitch/IO	nd[(2)]	0.3	3.8
soft pitch/HO	nd[(2)]	0.6	2.8

[(2)] nd : not determined, liquid at room temperature.

According to the results of Table I, the intermediate oils NO and WO, both rich in naphthalene, are the most efficient materials for QI extraction by the centrifuge process. The soft pitches obtained by processing with NO and WO presented 0.3 and 0.2 % QI, against 0.7 % presented by samples treated by quinoline, considered as a standard solvent for this process.

Since the heavier solvents IO and HO used in this study present boiling points higher than the SP distillation temperature (300°C), the presence of these solvents has been detected in the final products. This is the reason that the QI concentration in these materials is lowered and they were not considered appropriate solvents for this process.

The comparative analysis of SP, QI and TI of pre-treated and untreated soft pitches indicates that : a) the distillation treatment alone produces polymerization of all components, enhancing the value of all measured characteristics; b) phenolic oils produce selective reaction of toluene soluble molecules to increase the TI fraction, which in turn raises the SP, even when the QI are extracted; c) Quinoline, NO and WO induce the overall transformation with TI fractions becoming partially soluble while other compounds enlarge its molecular weight and enhance the SP of the pitches.

Conclusions

The complex technique used for the characterization of oils associated to the pre-prepared soft pitches indicated that the most efficient oils for QI extraction from pitch are naphthalene based (NO and WO).

The present methodology does not allow the complete extraction of primary QI fraction, but intermediary oils allow one to extract QI up to 90% of the initial concentration and produce physicochemical modification according to the solvent characteristics.

Acknowledgment

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