4.1 Introduction

The present work concentrates on modification of petroleum pitch by chemical modification method. Chapter III describes the treatment of pitches with nitric acid. The other oxidizing agents are sulfuric acid, phosphoric acid etc. Therefore work was undertaken to study oxidation of pitches with sulfuric acid. Petroleum pitch in powder form was treated with Sulphuric acid for various concentrations (10 to 60 wt%) for 1hrs time periods at room temperature. The non-treated and sulphuric acid treated pitches were pyrolyzed at 450°C and 950°C. The 450°C heat-treated pitches were used for the microstructure analysis. The non-treated and sulphuric acid treated pitches were characterized for the softening point, quinoline insoluble, benzene insoluble and toluene insoluble content and coke yield at 450°C and 950°C. Yardim et. al.[80] reported on the modification of pitch using different oxidizing agent like Nitric acid, sulphuric acid, phosphoric acid, and hydrogen peroxide at 140°C and further heat treatment at 250°C. The pitch modified with sulphuric acid at 140°C and further heat treated at 250°C increase the softening point and coke yield. But when pitch is modified with sulphuric acid at room temperature it shows marked difference in the results. The softening point increases from 110°C to 150°C and remain constant on further increasing concentration of sulphuric acid. It means that the chemical treatment with sulphuric acid at room temperature increase the softening point up to 150°C, that the chemical reaction between the pitch and sulphuric acid at room temperature is slower than it carried out at 140°C.
4.2 Softening Point of Non-Treated and Sulphuric Acid Treated Petroleum Pitch

Chemical treatments with sulphuric acid influence the softening point of parent pitch. Figure 4.1 shows increase in softening point of the pitch treated for one hour with sulfuric acid of varying concentration. It shows that as the concentration of sulfuric acid increases the softening point of modified pitches changes from 110°C to 150°C. The sulphuric acid treatment to pitch raises the softening point upto 150°C at concentration of 30wt%. The pitch treated for more than 30wt% and upto 60wt% the softening point remain constant at 150°C, it means the pitch treated with sulphuric acid with higher concentration at room temperature is not much more effective as compared to nitric acid.
Figure 4.1. Variation of Softening point of petroleum pitch treated for 1hr with different concentration of sulphuric acid
4.2 Quinoline Insoluble, Benzene Insoluble, Toluene

Insoluble Content

The chemical treatment with oxidizing agent like sulphuric acid also affects the insoluble content, which is related to the molecular weight of the pitch. Like in nitric acid, the insoluble content of modified pitches were also carried out in organic liquid like quinoline, benzene, toluene at the boiling point. Figure 4.2 shows the insoluble content of the modified pitches modified with increased concentration of sulphuric acid. Sulphuric acid reacts with pitch molecules and crosslinks the molecules in the pitches. Sulphuric acid contains sulphur, which is added in the modified pitches that ultimately increase the amount of insoluble content. As seen from the figure it shows that the quinoline, benzene and toluene insoluble content increase as the concentration of sulphuric acid increases.
Figure 4.2. Insoluble content of petroleum pitch treated for 1hr with different concentration of sulphuric acid
4.3 Coke Yield of Non-Treated and Sulphuric Acid Treated Pitch

The parent pitch was modified with oxidizing agent sulphuric acid at room temperature for the analysis of effect of chemical treatment on the coke yield. The non-treated and sulphuric acid treated pitch were heat treated at 450°C in nitrogen atmosphere at a heating rate 20°C/hrs upto 150°C and then further heated to 450°C at heating rate 40°C/hrs for 1hrs soaking time periods. The 450°C heat-treated pitches were further heat treated at 950°C in nitrogen atmosphere at a heating rate of 40°C/hrs for 1hrs soaking time period. The percentage coke yield of non-treated and sulphuric acid treated pitch are shown in Figure. 4.3. Modification of petroleum pitches with sulphuric acid results in change in the chemical composition and hence changes the coke yield of the parent petroleum pitch.
Figure 4.3. Percentage coke yield of petroleum pitch treated for 1hr with different concentration of sulphuric acid at 450°C

Figure 4.4. Percentage coke yield of petroleum pitch treated for 1hr with different concentration of sulphuric acid at 950°C
4.4 Optical Texture of Resultant Semicokes from Non-Treated and Sulphuric Acid Treated Pitch

The optical texture observed with polarized light optical microscope is one of the most relevant characteristics of carbon materials because it is closely related to conductivity, thermal expansion, mechanical strength and graphitizability [29]. During pyrolysis of modified petroleum pitch, small molecules are decomposed into free radicals and subsequently forming large molecules. Different optical texture of petroleum pitches after carbonization can be achieved as the large molecules move and stake at the action of the force [76]. Optical texture of semicokes from petroleum pitch is shown in Figure 4.5. The petroleum pitch gives semicoke of optical texture with monochromatic units, classified as coarse-grained mosaics. Optical texture of semicokes of modified petroleum pitches change greatly compared with that of the coal tar pitch. Modification with sulphuric acid contributes to change in the optical texture of resultant semicokes which are inhibiting the flow domain anisotropy, domains and coarse-flow anisotropic elongated. The modification condition i.e. concentration of oxidizing agents has great influence on formation of optical texture of resultant semicokes.

Figure 4.5(a) shows the optical texture of Semicoke of non-treated petroleum pitch, which shows a flow type behaviour means the development of the liquid crystal and formation of mesophase structure with large domains. When the pitch is treated with 10 wt% sulphuric acid it shows some change in formation of mesophase. Figure 4.5(b) shows the optical texture of Semicoke of 10 wt% concentrated sulphuric acid treated pitches for 1hrs. It shows the inhibition of development of flow structure due
to the acid treatment with sulphuric acid. As the concentration of sulphuric acid increases the texture of the modified pitch changes. Figure 4.5(c) shows the optical texture of 20 wt% concentrated sulphuric acid treated pitch for 1hrs. It shows coarse domain structure. As the concentration increases to 30, 40, 50 and 60 wt% the structure changes from coarse mosaic to fine mosaic structure. This change in structure occurs due to the inhibition of movement of the molecules and it did not allow to coalescence the mesophase and as a result the small domains of the pitch molecules occur. As the concentration increase the dehydrogenation and dehydrocondensation of the pitch molecules also occur inhibiting the formation of mesophase.
Figure. 4.5(a) Optical micrograph of non-treated petroleum pitch

Figure. 4.5(b) Optical micrograph of 10% conc. sulphuric acid treated petroleum pitch heat-treated at 450°C in N₂.
Figure. 4.5(c) Optical micrograph of 20% conc. sulphuric acid

Figure. 4.5(d) Optical micrograph of 30% conc. sulphuric acid treated petroleum pitch heat-treated at 450°C in N₂.
Figure 4.5(e) Optical micrograph of 40% conc. sulphuric acid treated petroleum pitch heat-treated at 450°C in N₂.

Figure 4.5(f) Optical micrograph of 50% conc. sulphuric acid treated petroleum pitch heat-treated at 450°C in N₂.
Figure 4.5(g) Optical micrograph of 60% conc. sulphuric acid