Turkish Asphaltites an Indigeneous Pitch for Carbon Materials

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Suitability and favourable economics of naturally occurring pitch asphaltites may prove to be a new opportunity for carbon material production. Generally asphaltic materials are formed by the migration of petroleum and solidification. During and after the migration due to tectonic movements, petroleum loses its light components, cracks into gas and undergoes a series of complex chemical and physical changes. The change from liquid to solid hydrocarbon is termed as metamorphisis not only under the influence of time, heat and pressure, but also as the result of complicated chemical, physical and biological processes[1].

The Mineral Research and Exploration Institute has determined over 60 million tons of asphaltite reserves in different areas in Turkey. Average values for the asphaltite reserves are reported to be water (1– 5.3 wt%), ash (33–45 wt%), sulfur (4.1–6.4 wt%), volatile matter (24–40 wt%), fixed carbon (47–59 wt%), hydrogen (3.2–5.6 wt%), and solubility in CS_2 (4.9–30 wt%)[2]

The mineral content of Turkish asphaltites, constituting as high as 45%, is a mixture of over 20 elements and minerals which are well incorporated with the organic matrix and may cause some treatment difficulties and at the same time may provide some inherent advantages. U_30_8 , V, Mo and Ni are the most abundant ones having concentrations of 0.29, 4.76, 4.15 and 2.89 kg/ tonne of Avgamasya asphaltite. The minerals are mainly carbonates, sulphates, and silicates. By using appropriate deashing procedures different ash contents may be obtained to be used for different purposes.

Due to the crude oil origin of the asphaltites many studies on solvent extraction with different solvents, mild pressure extraction, supercritical extraction, on virgin and demineralised samples were investigated by various researchers in Turkey and elsewhere. Pyrolysis of Turkish asphaltites using Fisher, Heinze, fluidised bed and fixed bed retorts are also investigated.

Studies on the bitumen obtained by solvent extraction of Turkish asphaltites resulted in the presence of a very large number of individual components which vary both in molecular type and size; thus the range of molecular weights vary between 200 and over 2000 for the oil fractions and between 1000 and over 5000 for the asphaltenes. [1]

Geochemical studies on the extracted products yielded that The Jurassic/Cretaceous oils of Turkey belong to the aromatic-intermediate principal class of oils; they contain up to 30% asphaltenes, between 40% and 70% aromatics and are rich in sulphur. Alteration of aromatic-intermediate oils during migration yields aromatic-asphaltic oils, volatile compounds are lost by biodegradation and both this and oxidation yield heavy, viscous or solid oils which contain up to 9% sulphur and as much as 60% asphaltenes. These sulphur compounds are formed by bacterial action, reaction of hydrocarbons with sulphur, inorganic oxidation or enrichment by evaporation and water washing. On the other hand, pyrolysis tended to produce a greater proportion of paraffinic products, asphaltenes and large polar aromatic fractions.

After 1990s some of the studies on asphaltites shifted to carbon products, such as activated carbon, carbon fibers and carbon foams. The carbon fiber studies were based on the solvent extracts and polyrolytes modified by solvent extraction, vacuum distillation and air blowing one by one, or as different combinations of them to obtain suitable pitch for environmental carbon fiber production. The carbon foam studies were performed on indigeneous asphaltite and three stage demineralised asphaltite samples. [3]

Asphaltite tar contains Quinonline-insoluble (QI) material which accelerates the formation of mesophase in the pitch and therefore lowers the quality of the fibres. In order to obtain better carbon fibre spinnability, QI free asphaltite tar was first extracted with pyridine and filtered to remove the pyridine insolubles and then distilled to obtain QI free asphaltite tar pitch prior to vacuum distillation. The vacuum distillation of tar was carried out at a pressure of 5 torr and at temperatures of 320, 340 and 410°C for 60 minutes. The pitches obtained at the three corresponding temperatures were coded as AVD1, AVD2, and AVD3, the softening temperatures for these pitches were determined to be 70, 134 and 171 °C respectively. For the case of solvent extracted asphaltite pitches reached to relatively higher softening temperatures of 132 °C for HI-BS and 220 °C for HI-THFS. Among these modified pitches HI-BS was very good spinnable, AVD3 was average spinnable and AVD1 AND AVD2 were non-spinnable.

ITU Carbon group was engaged in carbon foam production from a Japanese Mitsubishi AR pitch. The best performance was achieved at 293 °C, 5 sec pressure release time and 68 bar pressure. Under these conditions a compressive strength of 3.3 MPa was the maximum achieved. Using the data gathered on Avgamasya asphaltite over the years it was obvious that this metamorphised crude origined mineral is a natural pitch, therefore it was used as a precursor for carbon foam production. Pressure range of 1-9.8 Mpa, temperature range of 773-873 K and pressure release time range of 5-600 sec were used. Also original (41% ash) 26 % ash,10 % ash and 8 % ash Avgamasya Asphaltite samples were used as precursors.

Increasing the system pressure resulted in increasing the porosity, density and compressive strength of the foam. Furthermore, improvements in the foam structure in ligament, junction and wall formation were observed with pressure increase. Similar behaviour is also observed for the asphaltite foams for the temperature change. Pressure release time did not have a significant effect on density but had a substantial effect on the compressive strength of the asphaltite foam. Soak time had similar effect on the asphaltite foam as pressure and temperature comparatively in much less intensity level. Carbonisation caused a substantial increase in the compressive strength of the asphaltite foam in which both inorganic and organic changes played a role. Mineral matter increased the compressive strength tremendously. Also the effect of carbonisation surpassed the positive effect of mineral matter since the compressive strength increase was much more effective at lower mineral matter samples, except for the 10 % mineral matter case which implies a chemical composition effect.

References

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