INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

Pervasive requirement and utilization of reliable and readily available energy sources have led to the progressive depletion of conventional fossil fuel reserves. This has brought the unconventional fossil fuel reserves into focus. The unconventional petroleum resources are proven to hold a huge reserve around the world. One such resource is oil shale. Oil shale is a finely grained, porous, sedimentary rock which contains organic matter known as kerogen, concealed inside a mineral matrix. Kerogen is a complex organic compound which acts as the source of production of both conventional and unconventional petroleum and natural gases. On the application of heat, kerogen converts into bitumen which further breaks down into oil and gas. The most common and suitable method for production of oil and gas from oil shales as an alternative to conventional crude oil and natural gas is by retorting or pyrolysis. During oil shale pyrolysis process, the pyrolysis parameters significantly influence the yield and composition of the produced hydrocarbons. The mineral matters present in oil shale play a significant role in retorting or pyrolysis of oil shale. Inherent minerals such as silica, carbonate, pyrite etc. can drastically govern the heat transfer in oil shale, and influence the composition of products formed during pyrolysis of oil shale as an inherent catalyst.

The current work presents a comprehensive study on the pyrolysis mechanism of Indian oil shale. The collected oil shale samples were subjected different physicochemical, compositional, petrographic and thermogravimetric analysis. The oil shale sample were found to be of siliceous type, and sour in the presence of aliphatic, aromatic and phenolic compounds. Thermogravimetric (TG) analysis of the oil shale samples showed a total organic matter content of 21 wt%. The oil shale samples were subjected to different lab-scale pyrolysis experiments in novel pyrolysis reactors. The effect of pressure on the degradation kinetics and product yield and composition was studied. The kerogen was isolated from the oil shale sample to visualize the maturation of source rocks in the sub-surface. The oil shale samples were subjected to hydrous pyrolysis experiments to replicate the maturation of source rocks into hydrocarbons by geological phenomenon. Finally, the oil shale samples were blended with lignocellulosic biomass to study the catalytic effect of inherent minerals in the oil shale during co-pyrolysis process. The kinetic study of the oil shale and kerogen pyrolysis process was performed on TG data using three model-free isoconversional methods, viz. Friedman, Starink, and AIC method. The reaction mechanisms were determined using the Criado master plot. The average apparent activation energy for the pyrolysis process of oil shale and isolated kerogen showed activation energy values in the range of 216 kJ/mol to 247.54 kJ/mol. However, Under the pressurized condition, oil shale exhibited mean apparent activation energy values ranging from 341 kJ/mol to 451 kJ/mol with increase in pyrolysis pressure from 5 bar to 30bar. For the co-pyrolysis process, the mean apparent activation energy values were determined to be 249.5 kJ/mol for oil shale to rubber seed shell blend ratio of 1:2 and increased to 275 kJ/mol for blend ratio of 2:1. Lab-scale pyrolysis experiments of the oil shale samples were performed at atmospheric pressure using RSM optimization to identify the effect of process parameters on yield and composition of product products. This study showed maximum oil yield of 12.54 wt/wt% with 9.76 wt/wt% gas yield at the optimum condition of 600°C pyrolysis temperature and heating rate of 10°C/min, for particle size of 150 micron with holding time of 2 hours. High-pressure pyrolysis of the oil shale sample showed decrease in oil yield with increase in pyrolysis pressure and increase in concentration of gases due to cracking and the occurrence of secondary reactions. The results showed that kerogen initially matures into bitumen, and thereafter, gets converted to oil and gas in the presence of inherent minerals. A few targeted soaking and hydrous pyrolysis experiments were performed to simulate the in-situ maturation of source rocks during the catagenesis process in the sub-surface. Further, co-pyrolysis of oil shale with lignocellulosic biomass was performed to study the catalytic effect to the inherent minerals present in the oil shale. To understand the synergy of the co-pyrolysis process, the pyrolysis parameters were optimized to maximize the oil yield and simultaneously lower the concentration of the -OH compounds in the produced pyrolytic oil.

Identification of the evolved products during oil shale pyrolysis showed presence of CH_4, CO_2, aliphatic C-H, aromatic C-H and sulfur oxide functional groups. The relative concentration of C_2-C_4 gases obtained at high pressure increased dramatically compared to atmospheric pressure. The oil samples produced during pyrolysis of oil shale were found to be aliphatic in nature with carbon number distribution up to C_{38}, however, High-pressure pyrolysis showed carbon number distribution up to C_{22}. SimDist analysis showed an increase in the percentage of lighter (gasoline) and middle (kerosene) fractions from 26.2 wt/wt% and 18.3 wt/wt% at 1 bar to 45.3wt/wt % and 47.2 wt/wt% at 30 bar, respectively. The oil produced from soaking and hydrous pyrolysis showed the evolution pattern of aliphatics, aromatics, and heteroatomic compounds during the formation of hydrocarbons in the sub-surface. Characterization of the pyrolytic oil obtained co-pyrolysis of oil shale with rubber seed shell showed that with increase in concentration of oil shale in the blend, the percentage of -OH compounds decreased in the oil samples. GC analysis of pyrolytic gases showed that with the increase in blend ratio (more oil shale), the percentage of C_3-C_5 gases increases. GC-MS analysis showed the carbon number of the produced oil samples to be in the range of C_6 to C_{22}. The aliphatic content in the pyrolytic oil increased from 19.2 % to 31.15%, and –OH percentage decreased from 41.42% to 32.1% with increase in concentration of oil shale in the blend.