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From Refinery Residues to Carbon Fibre Precursors: Autoxidation-Driven Conversion of Vacuum Residue and HVGO

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ABSTRACT

Vacuum residue (VR) and heavy vacuum gas oil (HVGO) are the heaviest petroleum fractions and separated via vacuum distillation unit in refinery. These heavy fractions are very complex, and their market demand is shrinking due to complexity and associated cost to produce useful fuels. Yet these heavy fractions are rich in aromatic hydrocarbons, making them promising candidates for producing advanced carbon materials. There is an increasing interest in developing more economical carbon fibre precursors that can serve as alternatives to conventional polyacrylonitrile (PAN)-based precursors to meet the growing demand for lightweight, high-strength materials. However, it requires pretreatment to utilize them for carbon fibre production.

This study shows how VR and HVGO are being converted into carbon fibre precursors through controlled autoxidation. The approach focuses on promoting molecular growth within heavy petroleum fractions to produce the heavier aromatic structures. In the case of HVGO, controlled autoxidation at 190 °C, 72 h, limited oxygen availability with tetralin addition increased the asphaltenes content to approximately 47 wt%, while viscosity and softening point increased to about 117 Pa·s and 210 °C, respectively. Asphaltenes separated from oxidized HVGO were successfully melt-spun to produce green fibres with diameters of about 70 µm, which after stabilization and carbonization yielded carbon fibres with diameters of 40–50 µm and carbon contents above 90 wt%. Similar results were observed for vacuum residue. Controlled autoxidation increased the asphaltenes content of VR from roughly 20 wt% in the raw feed to nearly 77 wt%, while the softening point increased to around 190 °C. These structural changes enabled melt spinning of oxidized VR and VR-derived asphaltenes to produce green fibres with diameters in the range of 50–80 µm, followed by carbonization producing carbon fibres with carbon contents up to 92 wt%.

The results illustrate that autoxidation promotes cross-linked reactions that would lead to the

formation of heavier compounds with desired properties as carbon fibre precursors. For VR, it was possible to produce green fibre without separating solvent intensive asphaltenes separation steps. Although the results are promising, there are challenges associated with the processing including feedstock variability, the presence of heteroatoms and trace metals, and the need for improved control of precursor structure and fibre microstructure. Overall, controlled autoxidation can transform heavy petroleum fractions into spinnable precursors, highlighting a promising pathway for upgrading low-value refinery residues into high-value advanced carbon materials.

KEY WORDS

Vacuum residue; Heavy vacuum gas oil; Autoxidation; Asphaltenes; Carbon fibre precursors; Petroleum residue valorization

BIOGRAPHY

Dr. Muhammad Nurunnabi Siddiquee is an Assistant Professor in the Department of Chemical Engineering at King Fahd University of Petroleum & Minerals (KFUPM) and an affiliate of the Centre for Refining & Advanced Chemicals (CRAC). His research focuses on the valorization of petroleum fractions, particularly the controlled oxidative conversion of heavy petroleum streams into precursors for carbon fibres and other advanced carbon materials. He also works on converting light petroleum fractions into value-added products and *in situ* monitoring of dissolved oxygen during hydrocarbon autoxidation. His broader interests include multiphase oxidation in microfluidic reactors, asphalt hardening, and biofuel production from waste.

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