Deoxygenation of wheat straw fast pyrolysis vapors using HZSM-5, Al₂O₃, HZSM-5/Al₂O₃ extrudates, and desilicated HZSM-5/Al₂O₃ extrudates

HZSM-5 extrudates, its two constituents (HZSM-5 zeolite and alumina binder), and SiC for reference were tested after steam treatment for the upgrading of wheat straw fast pyrolysis (FP) vapors by an ablative bench scale system. In addition, mesoporosity was added to the HZSM-5 crystals of the zeolite/Al₂O₃ extrudates by desilication, which decreased the microporous volume and led to enhanced weak acidity and less strong acidity compared to the parent extrudates. For increasing biomass-to-catalyst ratios (w/w, B:C), oils were collected and analyzed for elemental composition, total acid number (TAN), moisture, molecular weight, evaporation characteristics, and chemical composition by gas chromatography mass spectrometry with flame ionization detection (GC-MS/FID), ¹H nuclear magnetic resonance (NMR), ¹³C NMR, and two-dimensional heteronuclear single-quantum correlation (2D HSQC) NMR. Compared to Al₂O₃, catalysts containing HZSM-5 promoted aromatization and limited the coke formation due to its shape selective micropores. Nevertheless, Al₂O₃ was effective in deoxygenation. At B:C ~7, 23 wt-% carbon/25 % energy recovery in the oil fraction was obtained while reducing the oxygen content by 45 % relative to a thermal reference oil fraction obtained over a SiC bed. As such, Al₂O₃ offers certain benefits compared to HZSM-5 based catalysts due to its lower cost and better hydrothermal stability with respect to acidity. At a catalyst temperature of 500 °C, the introduction of mesopores to HZSM-5 extrudates led to higher energy recovery as oil compared to the parent HZSM-5 extrudates. At B:C = 6.3, 23 wt-% carbon/26% energy recovery in the oil phase was achieved while removing 45% of the oxygen functionalities relative to the thermal reference bio-oil. Compared to deep deoxygenation for direct hydrocarbon production, mild deoxygenation improved the energy recoveries of the oil fractions and appears viable for pretreating pyrolysis vapors before co-processing bio-oils with fossil oil in refineries.

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