Continuous hydroprocessing of nitrogen-rich biocrudes from municipal solid wastes in a graded catalyst bed: Synergetic effect of oxygenates and nitrogenates

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Raising concerns regarding climate change produces an urge to decarbonize the long-haul transportation sector. In this regard, biomass could be a potential renewable source to produce sustainable, carbon-neutral liquid fuels. Hydrothermal liquefaction (HTL) followed by catalytic hydroprocessing is one of the most promising pathways to covert varying feedstocks (organic urban residues, forestry residues, algae etc.) into high quality renewable drop-in fuels. The energetically dense black viscous product from HTL ("biocrude"), contains a diverse organic pool with considerable amount of oxygen (~5-20%), nitrogen (~0-8%) and inorganic content (~0.1-0.6%). The presence of these organic contaminants poses new and exciting scientific challenges (e.g., thermal instability at high temperatures, coke precursors, extensive coking, nitrogen removal, exothermicity, pressure drops), which are indispensable to understand, during hydroprocessing. Therefore, special attention is needed not only to realize this complex biocrude mixture but also to optimally select proper hydrotreating temperatures in graded-catalyst reactor bed (three different types hydrotreating catalysts based on their porosity and nickel loading on γ-Al_2O_3 support) which can suppress coke formation and reactor plugging. In this work, we comprehensively discuss the missing scientific links which are essential in selecting proper hydrotreating temperatures in graded-catalyst rector bed and thereby, ensures smooth hydroprocessing with no coking for hundreds of hours (up to 600 hours).

A bench scale continuous hydrotreater (30-80 mL/h) with two reactors in a series was utilized. Based on the biocrude thermal stability, each reactor works at different temperatures and is packed with three different $NiMo/Al_2O_3$ commercial catalysts from Haldor Topsøe, to control exothermicity and pressure drop. TGA-DSC was used to determine the thermal stability of HTL biocrudes. Fourier-transform ion cyclotron resonance mass spectrometry (FT ICR MS), GCXGC-MS, GC-MS, inductively coupled plasma optical emission spectroscopy (ICP-OES), elemental analyzer (CHN/O) and higher heating value (HHV) were used for chemical characterization. Furthermore, the drop-in fuel products after true boiling point fraction distillation (ASTM D2892) underwent detailed characterization in accordance with ASTM D1655 (the global standard for aviation fuel) and EN 590 (European standard for diesel).

In brief, some of the main results that were obtained are:

1. **Oxygenates:** Oxygen functionalities are mostly related to thermal instability of biocrudes and extensive coking at higher hydrotreating temperatures. Both analytical (TGA-DSC) and experimental (extensive polymerization of sludge HTL biocrude) work evidently suggest that HTL biocrudes are thermally instable.
2. **Nitrogenates:** Over longer hydroprocessing times nitrogen functionalities (mostly basic nitrogenates) decrease the catalytic activity to a large extent at mild hydrotreating temperatures. Moreover, HTL biocrudes also have highly reactive organic species e.g., metalloporphyrins (analyzed via FT-ICR MS etc.), which extensively produce coking even at low hydrotreating temperatures.
3. **Selection of proper hydrotreating temperatures:** The vital key is to identify the coke precursors and have a comprehensive knowledge regarding thermal instability of given HTL biocrude.
4. **Overcoming the coking propensity:** Stabilization of highly reactive organic species under optimal hydrotreating conditions with carefully selected catalysts in a graded reactor bed.
5. **Complete nitrogen removal:** 100% nitrogen removal has been achieved for the first time during continuous hydrotreating (e.g., sludge biocrude). This milestone evidently paves the pathway and prospects of future aviation fuel approval from regulatory authorities.
6. **Compliance with ASTM D1655 and EN 590:** Chemical composition of produced fuels were analyzed by GCXGC-MS. The produced drop-in fuels after the fractional distillation of hydrotreated HTL biocrudes fulfill all specification of Jet-A1 and the stringent sulfur requirements in case of diesel (less than 10 ppm). The results of present work not only represent a great scientific advancement towards better understanding of HTL biocrudes and subsequent hydroprocessing step, but also paves the way toward green, sustainable and energy secure future where we can virtually utilize any kind of biomass source for drop-in fuels.

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