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Topic 10. Catalyst grading and knowledge of thermal stability: Two-front approach for smooth continuous hydroprocessing of hydrothermal liquefaction biocrudes

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Introduction

Hydrothermal liquefaction (HTL) of 2nd and 3rd generation biomass opens up an unparalleled opportunity by converting wet/dry organic content with no lipid restriction into a high quality biocrude. In the meanwhile, the HTL biocrude reveals a most exciting scientific challenge to produce sustainable drop-in biofuels for long haul transportation. Serious efforts from last two decades brought out some promising results, but so far successful long term continuous hydroprocessing remains a myth. Biocrudes from HTL not only contain high amounts of oxygen (O) but also relevant amounts of nitrogen (N). The O-containing compounds make the biocrude thermally unstable and enhance exothermicity during hydroprocessing. At the same time, N-containing compounds need higher temperatures for their removal during hydroprocessing.

To overcome the short coming from the present literature a novel method was defined and successfully used to understand much better the thermal stability of the HTL biocrude from *Spirulina* algae and the control of exothermicity during continuous hydrotreatment. A two-front approach was used during continuous hydroprocessing, where the **knowledge of biocrude thermal stability and the catalyst grading in the reactor bed (three different catalysts from low to high activity)** were utilized to stop coke formation and to control exothermicity. Overall impact of this work will **demonstrate for the first time, the results of a successful continuous hydroprocessing campaign (~ 350 h on stream)** for 3rd generation biocrudes. Finally, this rational approach produced real drop-in biofuels and successfully overcame the unforeseen challenges during continuous hydroprocessing of HTL biocrudes. This study will also document how the understanding and the choice of a right catalyst will make it possible to achieve rather ambitious targets.

Materials and Methods

A bench-scale continuous hydrotreater (30 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), GC-MS, inductively-coupled plasma optical emission spectroscopy (ICP-OES), elemental analyzer (CHN/O) and higher heating value (HHV) were used for chemical characterization.

Results and Discussion

Most of the studies on hydroprocessing of algae biocrudes are either batch or, if continuous, they report few data points and hydroprocessing end up with reactor plugging. Two-stage catalytic hydrotreatment of the given HTL biocrude with a graded catalyst bed showed complete deoxygenation and 92 % removal of nitrogen (7 wt.% N in feedstock) in upgraded samples. No sign of catalyst deactivation and reactor plugging due to coke formation was identified on the surface of the catalyst and catalyst bed. Smooth temperature profile with controlled exothermicity was observed during whole continuous campaign. Figure 1 shows the appearance of the upgraded fuels after the continuous hydroprocessing of *Spirulina* algae biocrude at different conditions i.e., weight hour space velocity (WHSV), temperature (T) and pressure (P). Drop-in fuels after the true-boiling point distillation showed on-spec metal content, density, pour point, cloud point and HHV for jet fuel and diesel. The present work exhibits that the right catalyst knowledge and better understanding of biocrude feedstock can pave the road toward green, sustainable and energy secure future.

Figure 1: Hydroprocessing of HTL biocrude from *Spirulina* algae in a two-stage reactor with graded catalyst bed operating at different conditions (i.e., WHSV, T and P).

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