Catalytic Upgrading of n-Butanol to Fully Synthetic Jet Fuel

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Project Goals: The Center for Bioenergy Innovation (CBI) vision is to accelerate domestication of bioenergy-relevant, non-model plants and microbes to enable high-impact innovations at multiple points in the bioenergy supply chain. CBI addresses strategic barriers to the current bioeconomy in the areas of 1) high-yielding, robust feedstocks, 2) lower capital and processing costs via consolidated bioprocessing (CBP) to specialty biofuels, and 3) methods to create valuable byproducts from the lignin. CBI will identify and utilize key plant genes for growth, composition and sustainability phenotypes as a means of achieving lower feedstock costs, focusing on poplar and switchgrass. We will convert these feedstocks to specialty biofuels (C4 alcohols, C6 esters and hydrocarbons) using CBP at high rates, titers and yield in combination with cotreatment, pretreatment or catalytic upgrading. CBI will maximize product value by in planta modifications and biological funneling of lignin to value-added chemicals.

Upgrading fermentation-based C4 alcohols (n-butanol or isobutanol) into fungible hydrocarbon fuels (e.g., jet, gasoline or diesel) is one promising alcohol-to-jet pathway as the olefin intermediates from C4 alcohols can be readily converted to jet-range hydrocarbons with a high selectivity. Currently there are only very limited reports or patents demonstrating that pure iso-butanol can be upgraded in a multi-step process of dehydration to isobutene followed by oligomerization to form iso-olefins as the dominant hydrocarbon fraction (1,2). The hydrocarbons produced from this prior approach have high number of branches, which limits the blending level into jet.

In this work, we target at upgrading of aqueous n-butanol to hydrocarbon fractions that are rich in n-paraffins and isoparaffins with low branches at much milder conditions – this will help to reduce the cost. This project will convert n-butanol to 1-butene rich olefins, which can be readily turned into jet-range hydrocarbons with larger fraction of n-paraffins and lightly branched paraffins (desired fraction in petroleum jet). Meanwhile direct one-step production of aromatic-rich blendstock will be investigated to produce the aromatic component.

We have found that 97% of butenes can be produced with ~100% n-butanol conversion over conventional H-ZSM-5 catalyst at 225 ºC and ambient pressure, where 1-butene is the dominating fraction among butene isomers. Increase of space velocity (1 to 8 h⁻¹) and n-butanol concentration (5.5 to 32%) did not show significant impact on n-butanol conversion, C3-C6 olefins selectivity and carbon number distributions, which offers potential to significantly reduce the reactor size. The mixed C3-C6 olefins were further oligomerized into longer-chain hydrocarbons over Amberlyst-36 catalyst at 150 ºC and 15 bar, leading to 70% of jet, 12% of gasoline and 10% of diesel fraction. The liquid hydrocarbons are rich in lightly branched iso-paraffins/olefins and n-paraffins/olefins, which offers great potential for higher blending. Catalyst development with 2D pillared zeolite is planned to further improve the selectivity of 1-butene and then to increase the quality of resulted hydrocarbon blendstock.
References

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