492e Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates

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Concerns about global warming, national security and the diminishing supply of fossil fuels are causing our society to search for new renewable sources of transportation fuels. Domestically available biomass has been proposed as a part of the solution to our dependence on fossil fuels; however the main obstacle to the more widespread utilization of our low-cost biomass resources is the absence of low-cost processing technology [1]. In this respect we are developing highly efficient aqueous-phase processing technology using heterogeneous catalysis for the conversion of biomass-derived carbohydrates into fuels and chemicals.

We have previously shown that a clean stream of light alkanes, ranging from C_1 to C_6, can be produced by aqueous phase dehydration /hydrogenation (APD/H) of aqueous sugar solutions [2]. The major disadvantage of this process is that the alkanes produced are not as valuable as a transportation fuel due to their high volatility. We have overcome this problem and are now able to selectively produce liquid alkanes ranging from n-C_7 to C_{15} by combining the dehydration/hydrogenation process with a C-C bond forming aldol condensation step [3]. Aldol condensation involves C-C bond formation of two molecules containing carbonyl groups. A number of molecules containing carbonyl groups can be derived from sugars including: 5-hydoxymethylfurfural (HMF), furfural, acetone, and tetrahydrofurfural (THF2A). Different molar ratios of these molecules were condensed by aldol condensation at room temperature using a mixed Mg-Al-oxide base catalyst to form large organic molecules. The reaction mixtures were then hydrogenated, using a 5% Pd/Al_2O_3 catalyst, to increase the aqueous solubility of these molecules and to minimize possible coking reactions that may take place from unsaturated molecules in the following step. The hydrogenated molecules were then converted into alkanes by dehydration/hydrogenation over a bi-functional catalyst (4 wt% Pt/SiO_2-Al_2O_3) containing acid and metal sites in a specially designed 4-phase reactor in which the aqueous organic reactant becomes more hydrophobic, and a hexadecane alkane stream removes hydrophobic species from the catalyst before they go on further to form coke.

The carbon selectivity for the cross-aldol condensation of HMF:Acetone shifted from a lighter alkane distribution (C_7 to C_9 alkane selectivity of 73 %) to a heavier alkane distribution (C_{13} to C_{15} alkane selectivity of 74%) as the molar ratio of HMF:Acetone was increased from 1:10 to 1:1. Condensation of furfural with acetone was used to produce liquid alkanes ranging from C_7 to C_{13} with 70% selectivity. Selective hydrogenation of the C=C bonds of furfural's heterocyclic ring yields THF2A, which is then self-condensed, followed by dehydration/hydrogenation to produce alkanes ranging from C_7 to C_{10} with 55% selectivity. The liquid alkanes produced are of the appropriate molecular weight to be used as a sulfur free diesel fuel additive, and contain 90% of the energy of the carbohydrate and H_2 feeds.

References

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