

Catalytic Production of Liquid Fuels from Biomass-derived Oxygenated Hydrocarbons

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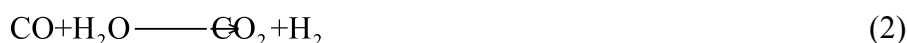
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The production of liquid fuels for the transportation sector is of importance for continued vitality of our industrialized society, because this sector requires fuels that burn cleanly and that have high energy densities for efficient storage at ambient conditions, criteria that are currently best fulfilled by petroleum, a non-renewable resource in diminishing supply. Furthermore, energy production from fossil fuels leads to emission of CO₂, a greenhouse gas that contributes to global warming. These issues associated with the continued combustion of petroleum by the transportation sector would be ameliorated by converting renewable biomass resources to clean burning liquid fuels having high energy densities.

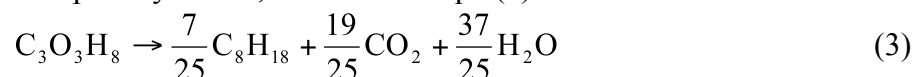
We summarize results in this presentation for the catalytic reforming of glycerol at low temperatures (*e.g.*, 550 K) to produce H₂/CO gas mixtures. Because this production of synthesis gas can be accomplished in the same temperature range as Fischer-Tropsch synthesis, the endothermic production of synthesis gas at low temperatures can be coupled with exothermic Fischer-Tropsch synthesis, leading to an energy-integrated process for conversion of biomass to liquid transportation fuels. The conversion of glycerol to H₂ and CO takes place according to the following stoichiometric equation:



The H₂:CO ratio for the above reaction is equal to 1.33, and this ratio can be increased by the water gas shift reaction:



The stoichiometry for conversion of glycerol to liquid alkanes, by the formation of synthesis gas coupled with Fischer-Tropsch synthesis, is shown in Eqn. (3):



This overall reaction to produce liquid fuels from glycerol is slightly exothermic, such that 96% of the energy content of the glycerol molecule is retained in the liquid alkane product.

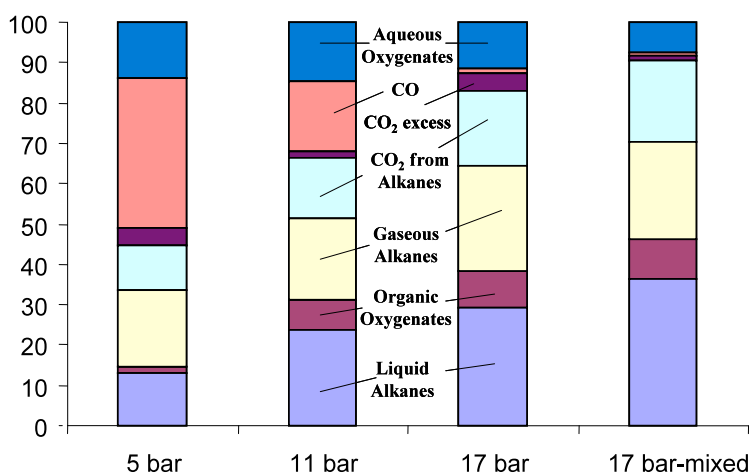


Figure 1. Effluent from glycerol conversion.

Figure 1 summarizes the results from studies of glycerol conversion to liquid alkanes at 548 K in our single-reactor catalytic process, achieved by the integration of glycerol reforming over PtRe/C

with Fischer-Tropsch over Ru/TiO₂. Three of the stacked bars in this figure are for a two-bed reactor arrangement consisting of PtRe/C upstream of Ru/TiO₂ at different pressures, whereas the bar designated as 17 bar-mixed consists of a single bed in which both catalysts are mixed (with a small upstream bed of PtRe/C to initiate H₂ production from glycerol). It can be seen that the percentage of the carbon leaving the reactor as liquid alkanes increases with increasing pressure, while the percentage of carbon leaving as CO decreases. For the mix-bed arrangement, it is apparent that approximately 35% of the carbon leaving the reactor is present as liquid alkanes, with another 10% present as hydrophobic oxygenates in the organic phase. Another 25% of the carbon leaves the reactor as gaseous alkanes. The gaseous effluent also contains CO₂, accounting for about 20% of the carbon leaving the reactor; however, most of this CO₂ was produced by the stoichiometric reaction involved in the conversion of glycerol to alkanes, and its production is unavoidable (see Eqn 3). Overall, approximately 90% of the carbon leaving the mixed-bed is present as alkanes, organic alcohols, and stoichiometric CO₂.

Figure 2 outlines a second approach of the present paper for the conversion of carbohydrates to alkanes with targeted molecular weights. The first step in this approach is the conversion of carbohydrates to compounds having carbonyl groups (-C=O), such as furfurals, ketones, and aldehydes. This conversion may be accomplished using chemical catalysts, such as the formation of furfural and hydroxymethylfurfural (HMF) by acid-catalyzed dehydration of xylose and fructose, respectively. Alternatively, these compounds can be formed biologically, such as the fermentation of glucose to produce acetone. These carbonyl compounds could also be formed by thermochemical processes, such as as pyrolysis or high pressure liquefaction.

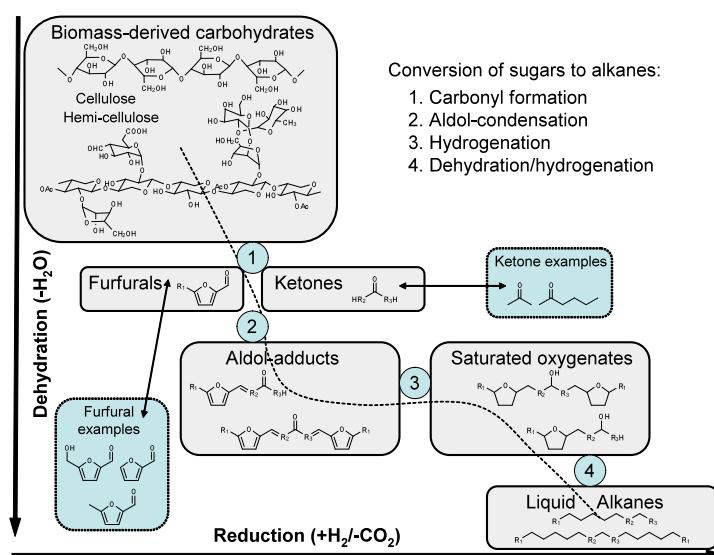


Figure 2. Targeted synthesis of alkanes from sugars.

The formation of carbonyl compounds from carbohydrates is followed by aldol-condensation reactions over basic catalysts to form C-C bonds. Figure 2 shows the crossed condensation between a furfural compound (F) and a ketone (K) to form F-K monomer and F-K-F dimer compounds. These C-C coupling reactions are accompanied by dehydration, leading to the formation of highly conjugated systems of C=C and C=O double bonds. Importantly, the relative amounts of F-K monomer and F-K-F dimer compounds formed in this step can be controlled by adjusting the relative amounts of the furfural and ketone reactants. The C=C bonds in these aldol adducts can then be hydrogenated over Pd-based catalysts, followed production of alkanes by a combination of dehydration and hydrogenation reactions over bifunctional catalysts containing metal and acid sites.